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Contents of Volume

Number 1

Vasilii Vladimirovich Korshak 1
A M Sladkov

Advances in the Synthetic Chemistry of Macromolecular Compounds 2
V V Korshak, N M Kozyreva

Advances in Acceptor-catalytic Polyesterification 16
V A Vasnev, S V Vinogradova

Some Structural and Chemical Aspects of Polycondensation 28
E Turska, S Boryniec, W Sulkowski

Block Copolymers of the Polycondensation Type 42
P M Valetskii, I P Storozhuk

Ladder Polyheteroarylenes — Progress and Problems 62
A L Rusanov

Synthesis of Polymers by Polycyclotrimerisation 79
V A Sergeev, V K Shitikov, V A Pankratov

Advances in the Production of Thermostable Antifrication Plastics 94
I A Gribova, O V Vinogradova

Number 2

The Carbon–Nitrogen Triad Prototropic Tautomerism 107
B A Shainyan, A N Mirskova

Investigation of Isotope Effects with the Aid of Kinetic and Catalytic Polarographic Currents 118
A Călusaru

Structural Rearrangements in Carbaboranes and Related Compounds 130
V I Stanko, V A Brattsev, S P Knyazev

Phosphorus Rings, Clusters, Chains, and Layers 153
V I Kosyakov, I G Vasil'eva

The Present State of the Quantitative Theory of Polycondensation Processes 162
S I Kuchanov, E B Brun

Trimerisation Polycondensation of Aromatic Acetyl Compounds and Their Ketals 189
M M Teplyakov

Oxidative Polymerisation of Vinyl Monomers 199
M M Mogilevich

Information 212
A M Sladkov

The "Nauka" Publishing House is Preparing for Publication a Collection of Articles "Sorbtsiya i Khromatografiya" (Sorption and Chromatography), 20 Sheets, Price 3 Roubles 212
A M Sladkov

Number 3

Dinuclear Iron Carbonyl Complexes with Nitrogen-containing Bridges 213
A N Nesmeyanov, M I Rybinskaya, L V Rybin

Lanthanide Titanates 228
L G Shcherbakova, L G Mamsurova, G E Sukhanova

Non-stoichiometry of the Alkaline Earth Metal Oxides 243
P V Kovtunenko, Ya L Kharif

Advances in the Study of the Stereochemistry of Quinolizidines, Indolizidines, and Pyrrolizidines 262
I M Skvortsov

Preparation and Reactions of Chloro-derivatives of Nitriles 282
E M Movsum-zade

Advances in the Chemistry of 1,2-Azoles 289
S D Sokolov

Electrochromism for the Investigation of Slow Movements in Macromolecules 306
F P Chernyakovskii

Number 4

Photochemical Methods for Recording Information. Primary Photoprocesses 317
M V Alfimov, O B Yakusheva

Catalytic Ionic Hydrogenation 332
M I Kalinkin, G D Kolomnikova, Z N Parnes, D N Kursanov

The Synthesis and Structure of Telluranes 343
I D Sadekov, A Ya Bushkov, V I Minkin

The Stability of Colloid Systems (Theoretical Aspects) 363
B V Deryagin

The Influence of Hydrogen Bonds and Ionic Interactions on the Properties of Carboxyl-containing Copolymers and Ionomers Based on Them 389
N G Marina, Yu B Monakov, S R Rafikov

Nuclear Magnetic Resonance Study of Polymer–Low-molecular-weight Substance Systems 404
A I Maklakov, V S Derinovskii

The Solvation of Mercury Ions and the Formation of Their Complexes in Water and Non-aqueous Solvents 418
L N Balyatinskaya

Number 5

A New Mechanism of Nucleophilic Substitution 431
I P Beletskaya, V N Drozd

Electrochemistry of Metal Chelates in Non-aqueous Media 449
G K Budnikov, T V Troepol'skaya

Dissociative Ionisation of Nitro-derivatives of Arenes and Heterocyclic Compounds 463
R A Khmel'nitskii, P B Terent'ev

Phosgene in the Chemistry of Organosilicon Compounds 473
V F Mironov, V D Sheludyakov, V P Kozyukov

The Etherates of Organoaluminium Compounds 487
V P Mardykin, P N Gaponik, A F Popov

Extraction of Heteropolycompounds and Its Application in Inorganic Analysis 502
E N Dorokhova, I P Alimarin

The Use of High-pressure Liquid Chromatography in the Analysis of the Structural Components of Nucleic Acids 517
V K Kagramanova, S N Bubenshchikova, L A Baratova

Number 6

The Oxygen Radical-anion $O_2^{\cdot}$ in Chemical and Biochemical Processes 527
I B Afanas'ev

Group-theoretical Methods in Quantum-chemical Calculations 550
I G Kaplan

Diazenium Salts 563
M A Kuznetsov

The Stereochemistry of Organoarsenic Compounds 582
F D Yambushev, V I Savin

Electrophotographic Phenomena in Linear Polymers with Saturated and Conjugated Bonds 596
Yu A Cherkasov, M I Cherkashin

Number 7

Excess Electrons in Non-polar Molecular Liquids 615
B S Yakovlev

Mass Spectrometry with Chemical Ionisation 631
A A Solov'ev, V I Kadentsev, O S Chizhov

Dinuclear and Polynuclear Complexes with Azomethine Ligands and Their Magnetic Properties 645
V A Kogan, V V Zelentsov, O A Osipov, A S Burlov

The Hydride Addition of Organohydrosiloxanes to Compounds with a Multiple Carbon–Carbon Bond 657
K A Andrianov, J Souček, L M Khananashvili

The Conformation of γ-Aminobutyric Acid and Its Analogues 669
I A Sytinskii, A T Soldatenkov

Advances in the Search for Medicinal Drugs Based on γ-Aminobutyric Acid 679
V M Kopelevich

The Reactivity of Aromatic Dialkenyl Compounds in Polymerisation Reactions 692
R M Nasirova, L S Murav'eva, E A Mushina, B A Krentsel'

The Sedimentation of Polydisperse Polymers 699
I K Nekrasov

Identification of Substances in Gas Chromatography 714
A A Anderson, M V Shimanskaya

Number 8

The Use of Spin-trapping in the Study of the Mechanisms of Radical Processes 729
V E Zubarev, V N Belevskii, L T Bugaenko

Donor–Acceptor Interactions between Non-silver Information Recording Processes 746
A D Grishina, A V Vannikov

The Insertion of Diene Hydrocarbons in a Transition Metal–Ligand Bond 758
M I Lobach, V A Kormer

Application of Ion-exchange Resins in Photometry 774
F I Lobanov, G K Nurtaeva, N V Makarov

Diffusion of Electrolytes in Polymers 781
A L Iordanskii, A L Shterenzon, Yu V Moiseev, G E Zaikov

Non-isothermal Processes and Methods of Investigation in the Chemistry and Mechanics of Polymers 798
A M Stolin, A Ya Malkin, A G Merzhanov

Number 9

Aleksandr Nikolaevich Nesmeyanov 813
A M Sladkov

Progress in the Theory of Acids and Bases 814
M I Kabachnik

The Isomerisation of Unstable Organoelemental Radicals in Liquid-phase Reactions 828
R Kh Freidlina, A B Terent'ev

NMR Study of Equilibrium Intermolecular Exchange Processes Involving Univalent Organometallic Groups of the Type R_nM, Containing an Atom of a Heavy Non-transition Metal from Periods V and VI 840
L A Fedorov, A S Peregudov, D N Kravtsov

Hydrogen Bonds and the Reactivity of Organic Compounds in Proton Transfer and Nucleophilic Substitution Reactions 854
L M Epshtein

Reactions of Copper and Silver Organoacetylides 868
A M Sladkov, I R Gol'ding

Plasteins. Their Preparation, Properties, and Use in Nutrition 897
V M Belikov, M Yu Gololobov

Number 10

Dynamics of Elementary Processes in Liquids 913
A L Buchachenko

Structure of the Electrical Double Layer in Non-aqueous Solvents 932
B B Damaskin, R V Ivanova

Hydroxamic Acids and Their Metal Complexes 948
Y K Agrawal

Mixed Organic Derivatives of Mercury and Silicon 964
M G Voronkov, N F Chernov

Molecular Weight Distribution in the Production of Homopolymers 979
N S Enikolopyan, R G Gleizer

Activators of the Anionic Polymerisation of Lactams 991
T M Frunze, V V Kurashev, V A Kotel'nikov, T V Volkova

Analysis of Atmospheric Pollutants by Gas Chromatography 1006
Yu S Drugov, V G Berezkin

Number 11

Artificial Light-sensitive Enzymatic Systems as Chemical Amplifiers of Weak Light Signals 1027
I V Berezin, K Martinek

The Influence of the Solvent on the Rates of Chain Propagation and Termination Reactions in Radical Polymerisation 1040
V F Gromov, P M Khomikovskii

Inorganic Radical-ions and Their Organic Reactions 1055
A F Morkovnik, O Yu Okhlobystin

Association of Dye Molecules and Its Spectroscopic Manifestation 1076
V I Yuzhakov

Kinetics and Catalysis of the Oxidation of Titanium, Silicon, Germanium, and Gallium Arsenide 1092
N P Peksheva, V M Strukov

Reactions in a Protein–Polymeric Carrier System Used for the Immobilisation of Enzymes 1109
M I Shtil'man

The Synthesis and Properties of Polymeric Azaporphin Compounds 1125
A A Berlin, A I Sherle

Number 12

Some Problems of the Chemical Physics of the Ageing and Stabilisation of Polymers 1139
N M Emanuel'

Thermochemical Studies Necessary for the Selection of Key Thermodynamic Quantities 1168
V A Medvedev, I L Khodakovskii

Advances in the Thermodynamics of Organic Compounds in the USSR 1174
I B Rabinovich

Exciting Developments in the Thermophysics of the Pnictides and Chalcogenides of the Transition Elements 1186
E F Westrum Jr

Infrared Spectroscopy of the Hydrogen Bond as a Method for the Investigation of Intramolecular Interactions 1198
A N Egorochkin, S E Skobeleva

The Formation of Coatings in the Anodic Electrodeposition of Water- Miscible Lacquer Systems 1212
P I Zubov, I A Krylova

Transformations in Refractory Compounds, Brought about by High Pressures and Temperatures 1225
Yu G Zainulin, S I Alyamovskii, G P Shveikin

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Advances in the Synthetic Chemistry of Macromolecular Compounds

V.V.Korshak and N.M.Kozyreva

The individual stages in the development of the synthetic chemistry of polymers are examined in their historical aspect. The present state of the chemistry of macromolecular compounds and the prospects for its development in the future are discussed and the types and characteristics of monomers used in polymerisation and polycondensation are considered. The entire wide variety of known polymeric macromolecules arising in various syntheses of polymers is demonstrated. Attention is drawn to the fundamentally important fact that all reactions involving the synthesis of macromolecular compounds lead to the formation of heterounit polymers, and the necessity to take into account the heterounit nature of polymers when problems of the dependence of their properties on their structure are considered is pointed out. Certain problems arising in modern technology and involving tasks soluble by synthetic methods are described and questions concerning the synthesis of polymers with specific properties are considered in relation to a number of examples. The present level of development of the syntheses of polymers by polymerisation and polycondensation methods and by the modification of existing polymers is described. The varieties of polymerisation and polycondensation processes and of the modification of existing polymers are examined (mainly in relation to new reactions, primarily those which lead to the formation of polymers of a new type). The increasing tendency towards the synthesis of polymers with specific properties, which is apparent at the present time, is emphasised.
The bibliography includes 122 references.

CONTENTS

I.	Introduction	2
II.	The present state of the problem of the synthesis of polymers	3
III.	The heterounit nature of polymers	4
IV.	Problems of the synthesis of polymers with specific properties	5
V.	Polymerisation	7
VI.	Polycondensation	10
VII.	Modification of polymers	12

I. INTRODUCTION

The chemistry of macromolecular compounds is at the present time one of the most vigorously developing branches of chemistry. The rapid rate of its development can be accounted for by the fact that the synthetic chemistry of polymers ensures the growth of important branches of polymer technology involving the manufacture of plastics, synthetic rubber, synthetic fibres, and synthetic film-forming materials. The production of these materials plays in its turn an important role in the development of many of the most important branches of new engineering and modern industry: aviation, automobile, electro- and radio-technical, machine construction, building, etc. industries.

It may be assumed that the synthetic chemistry of polymers was initiated in 1833 [1] when Berzelius [2] formulated the concept of polymerisation, which has persisted, with some modification, to the present day. Gay-Lussac [3] obtained the first synthetic polymer—a polylactide based on lactic acid, and Braconnot [4] obtained cellulose nitrate, having achieved for the first time a polymer-analogue reaction. During the 145 years since then, the field of macromolecular compounds has been enriched by a large number of new synthetic methods and polymers of different structures. At the same time, theoretical ideas concerning the mechanism of the synthesis of polymers and the characteristics of their structure and properties have been developed. Studies of Staudinger, Carothers, Flory, Natta, and others have been very important in the formation of modern concepts concerning polymers. Russian and Soviet scientists made a significant contribution to the development of polymer chemistry. The studies by Butlerov, Lebedev, Favorskii, Shorygin, Kargin, Andrianov, Medvedev, Petrov, Korotkov, Ushakov, and others laid the foundations of polymer science and technology.

The first reports of the synthesis and investigation of macromolecular compounds described the results of random successes until the investigations of Butlerov, Kekulé, and Cooper led to the creation of the structural theory of organic chemistry [5]. The elegant edifice of polymer science was subsequently created on its basis. A huge army of investigators are now concerned with the synthesis, study, and applications of new polymers: 50% of organic chemists work directly or indirectly in the field of polymers, developing new methods for the synthesis of monomers, plasticisers, initiators, inhibitors, and other substances used in the synthesis and investigation of polymers. Many investigators are occupied with the synthesis and study of polymers and an even greater number of workers deal with the application of the results of these studies in industry, where polymers are manufactured, processed, and applied. To illustrate the wide scale of studies on the synthesis of polymers, one may say that during one year about 50 000 new polymers are now synthesised, i.e. more than 160 new polymers every day or one new polymer in each 3 min. [6] This has now led to the synthesis of hundreds of thousands of various polymers, but, despite this, the rate of synthesis increases continuously each year.

The explanation is that it is precisely in the field of synthesis of polymers that the efforts of investigators have been most effective both for the developments of the theoretical foundations of polymer science and for industry, enriching it in new polymeric materials. One is therefore fully justified in claiming that the synthetic chemistry of polymers constitutes a strategic component of the development of polymer science.

The industrial production of polymers is developing just as rapidly. The world production of polymers of all types has recently exceeded 64 million tons, approaching the scale of the manufacture of steel [7].

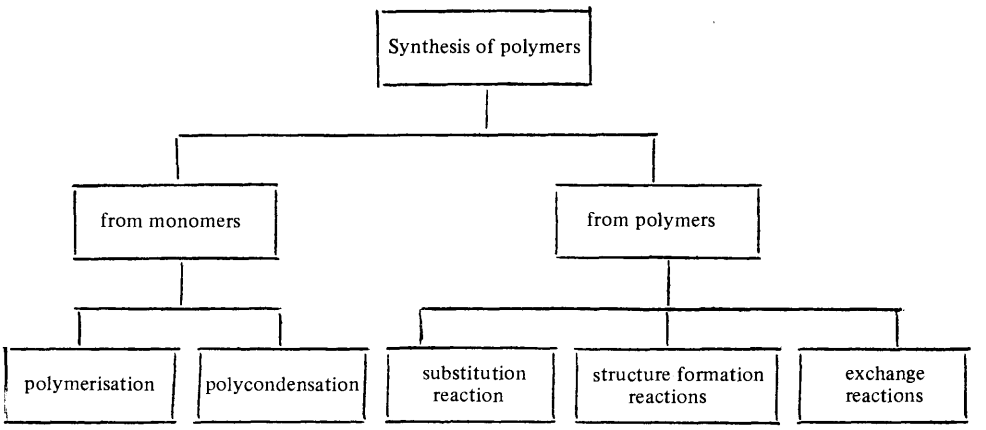


Figure 1. Scheme illustrating the fundamental ways of synthesising polymers.

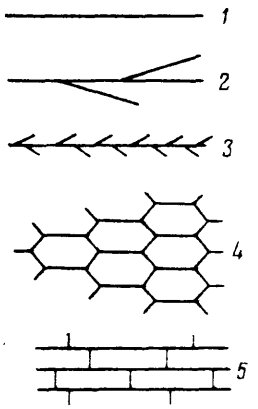


Figure 2. Shapes of macromolecules: 1) linear; 2) branched with a small number of long branches; 3) branched with a large number of short branches; 4) planar, parquet-like; 5) three-dimensional.

II. THE PRESENT STATE OF THE PROBLEM OF THE SYNTHESIS OF POLYMERS

Macromolecular compounds may be synthesised in several ways, as shown in Fig. 1. It is seen from the scheme that there are two types of synthesis of polymers: the first pathway involves the synthesis of polymers from low-molecular-weight substances by polymerisation and polycondensation and the second involves the modification of existing polymers by substitution, structure-formation, and exchange reactions.

We shall examine the present state of each of these types of synthesis in conformity with the above scheme. In the first place one should note that the advances in the synthesis of macromolecular compounds led to the formation of a wide variety of polymeric structures. As a result of the development of synthetic methods, it is now possible to obtain a wide variety of different forms of macromolecules, as shown in Fig. 2, where linear, planar, and three-dimensional forms of molecules known at the present time are illustrated. It is noteworthy that each of these forms also includes macromolecules of different types. Thus linear macromolecules may be of at least several types (Fig. 3). We see that the linear structure of the macromolecule is made up in different ways from units consisting of individual atoms or whole groups.

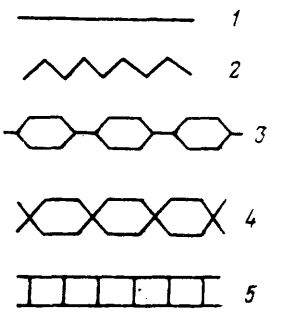
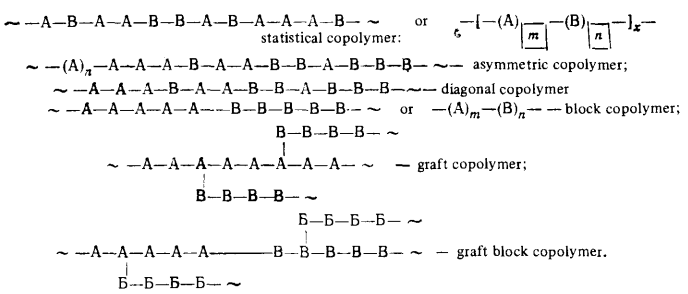


Figure 3. Forms of linear macromolecules: 1) straight ("carbene"); 2) zig-zag; 30 cyclochain; 4) cyclospiran; 5) ladder like.

There is also a wide variety of structures of macromolecular chains, particularly in different copolymers. Fig. 4 shows that the integral composition of the macromolecular chain varies along its length in various types of copolymers, starting from the usual statistical copolymers and extending via copolymers with macromolecular compositions varying along the chain (diagonal and asymmetric copolymers) to block and graft copolymers[8]. The structures of these copolymers can be represented by the

following formulae



The appearance of an increasing number of "hybrid" polymers, which are synthesised both by polymerisation and polycondensation or by the modification of existing polymers with the aid of polymerisation or polycondensation methods, should also be noted [6]. An example of "hybrid" polymers is provided by the hardening of unsaturated polyesters, which are obtained in the first stage by polycondensation, while in the second stage they copolymerise with styrene and other unsaturated monomers to form a three-dimensional copolymer [9]. Similarly, unsaturated polyamides, obtained by the polycondensation of fumaryl chloride with *N*-alkylated aromatic diamines, copolymerise with vinyl monomers to form copolymers with three-dimensional structures [10,11].

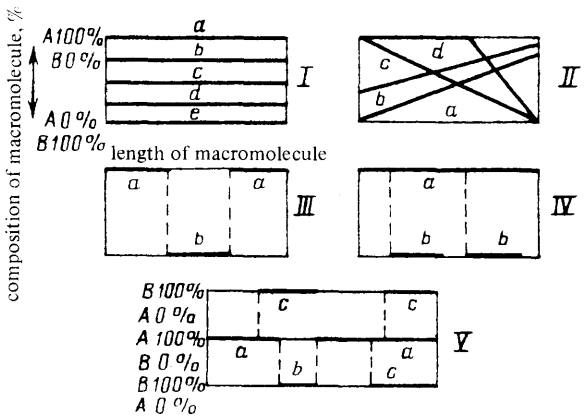


Figure 4. Variation of the integral composition along the length of the macromolecule in various copolymers: I) usual copolymers (*a*, *b*, *c*, *d*, *e*); II) variable-composition copolymers (*a*, *b*), diagonal copolymer (*c*), asymmetric copolymer (*d*); III) block copolymer [*a*) block consisting of A units; *b*) block consisting of B units]; IV) graft copolymer [*a*) main chain consisting of A units; *b*) grafted chains consisting of B units]; V) graft block copolymer [*a*) blocks consisting of A units; *b*) block consisting of B units; *c*) grafted chains consisting of B units].

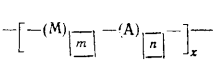
Certain polyamides are synthesised by the polycondensation of diamines with dicarboxylic acids, after which they are copolymerised with epoxy-compounds to form graft copolymers of the polyamide and epoxyalkanes [12]. Finally, block copolymers are synthesised by the reaction of poly(ethylene oxide), obtained by the polymerisation of epoxyethane, with poly(ethylene terephthalate) [13].

The wide variety of the structures of polymers, which is manifested particularly clearly in the case of copolymers, may be illustrated in relation to polypeptides. The exceptional complexity of the synthesis of polymers is associated, among other causes, also with the fact that in many instances there is a possibility of the formation of an unlimited number of isomers, since the 20 aminoacids encountered in natural proteins can form 10^{1200} macromolecules with different structures for a molecular weight of 100 000 (which corresponds to a polarisation coefficient of approximately 1000). In order to grasp the significance of this number, we may recall that the number of atoms of all the elements in the entire terrestial sphere is 10^{50}.

The enormous influence of the purity of the initial monomers on the course and result of the synthesis of polymers was established during research. The presence of impurities during polymerisation causes early chain termination, the branching of macromolecules, the formation of various unstable groups, and the formation of heterounit polymers as a result of these reactions. The presence of impurities in polycondensation also lowers the molecular weight of the polymers and leads to the formation of terminal groups of a different type, the branching of macromolecules, and other reactions leading to a heterochain polymer. Thus, since impurities as a rule are not inert in relation to the synthesis of polymers, they induce an uncontrollable modification resulting in the formation of heterounit polymers [14,15].

III. THE HETEROUNIT NATURE OF POLYMERS

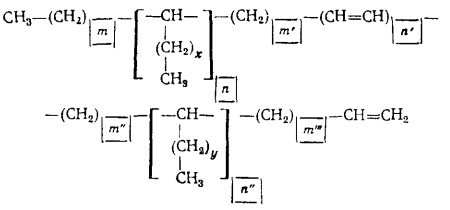
The side reactions caused by the presence of various impurities as well as side reactions of all other types (for example, isomerisation, polymerisation, branching, etc.) alter the structure of part of the polymer units and lead to the formation of anomalous units, which produces heterounit polymers [16]. Fig. 5 presents examples of various reactions leading to the formation of anomalous units in the macromolecule and of heterounit polymers. Because of these causes, heterounit polymers having the general formula



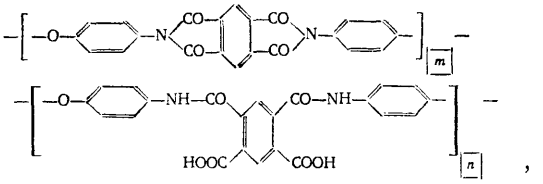
where M is a normal unit and A an anomalous unit and m and n are coefficients indicating a statistical distribution of units, are formed in all syntheses of polymers by polymerisation and polycondensation methods [14-16]. Polymer modification processes (substitution, vulcanisation, and exchange reactions) also lead to the formation of heterounit polymers [15]. For this reason, a study of the formation of a heterounit macromolecule and of its microstructure is a most important task in polymer science, since only in this way can one solve the problem of the synthesis of polymers with a set of properties specified beforehand [15]. The establishment of exact relations between the structure and properties of polymers will be possible only when all the details of the structure of macromolecules and their mutual influence become known.

The enormous importance of the heterounit nature of polymers as a factor which influences significantly the entire set of their chemical and physical properties has been demonstrated in many instances [16]. This is particularly significant in view of the fact that heterounit polymers constitute at present the dominant form of polymeric

structures. For this reason, the formula of a real polymer should take into account its heterounit nature and the presence of anomalous units. Consequently the real formula of polymers such as polyethylene, expressing its heterounit nature, is as follows[17]:



It clearly differs markedly from the idealised formula $-[CH_2-CH_2]_X-$ usually employed. The heterounit polyimide, containing non-cyclised units, whose real formula is



constitutes yet another example.

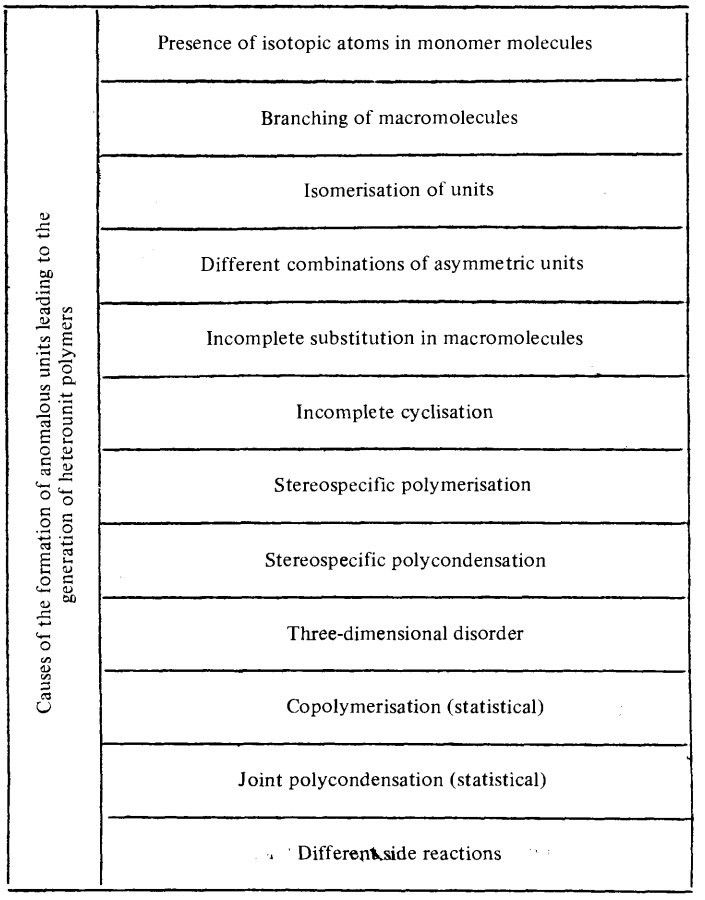


Figure 5. Causes of the formation of anomalous units leading to the generation of heterounit polymers.

In addition, the properties of polymers are influenced by the presence of the isotopes of hydrogen, carbon, and other polymer-forming elements. Thus it has been shown[18] that the replacement of hydrogen by deuterium in polyethylene alters appreciably physical characteristics such as density, melting point, glass point, yield point, and chemical properties. On this basis, it was concluded that the presence of isotopes in macromolecules leads to the formation of heterounit polymers, which affects the entire set of their physical and chemical properties. At the same time, account must be taken of the possibility of the simultaneous operation of the isotope effect and of the influence of the anomalous units arising as a result of branching, isomerisation, and other chemical reactions—these effects may coincide and enhance one another. The heterounit nature of polymers should be manifested particularly significantly in biopolymers, where one may expect very specific and very appreciable manifestations of the isotope effect. In fact, we know that, in structures such as proteins, nucleic acids, etc., very small structural changes influence significantly the biological functions. At the same time it is known that various isotopes are non-equivalent in their physiological properties. Thus, among the causes responsible for the heterounit nature of polymers, one must also point to the influence of the presence of stable isotopes in the molecules of the initial monomers and polymers.

IV. PROBLEMS OF THE SYNTHESIS OF POLYMERS WITH SPECIFIC PROPERTIES

Investigators working in the field of the synthesis of polymers are faced by complex tasks. These include tasks associated with the development of new and the improvement of existing methods for the synthesis of polymers in order to increase their yields and to improve the physicochemical characteristics of polymers and the articles made from them. At the same time problems concerning the application of methods of polymer chemistry to the synthesis of new polymers with the required set of properties, which are of practical interest and are essential for the execution of a particular task, are being solved. We shall consider certain examples of the synthesis of new polymers with specific properties.

The preparation of polymers with many practically important properties such as high heat resistance and thermal stability, non-combustibility, resistance to light, and specific electrophysical and other properties, constitutes an enormously important task[19-21]. An important branch of the synthesis of polymers involves the preparation of thermostable polymers capable of being used for a long time at high temperatures[19-22,23]. Many polymers have been synthesised for this purpose, including polyorganosiloxanes, particularly those with a ladder structure, and polyheteroarylenes, particularly polyimides, and similar structures[19,22,24,25]. Among these, polyamides based on pyromellitic anhydride and di-(4-aminophenyl) ether as well as polyoxadiazoles, polybenzimidazoles, and polybenzoxazoles proved to be particularly interesting. They are of practical interest as the starting materials for the manufacture of thermostable fibres and films. Studies on polymers for different electrotechnical purposes have been greatly developed: polymers for the manufacture of insulators, electrically conducting materials, semiconductors, polymers with photoelectric activity, etc. Many investigators have devoted much attention to the problem of the synthesis of polymeric

semiconductors and superconductors. Polymers with conjugated bonds of the polyvinylene, polyacetylene, polyphenylene, etc. type as well as polyheteroarylenes and their derivatives are obtained for this purpose [26].

The problem of the protection of the environment has faced synthetic chemists with the problem of the preparation of polymers capable of being decomposed after their utilisation, which is particularly important for packing materials. This problem is being solved in different ways, among which one of the most important is the synthesis of polymers capable of being decomposed by light. For this purpose, groups are introduced into the macromolecule increasing its sensitivity to light. On the other hand, practical problems necessitate the synthesis of noncombustible and self-extinguishing polymers, which is particularly important for the building industry and many branches of modern technology [27]. The preparation of composite and other materials with a high strength is likewise especially important [28-31]. The advantages of strengthened [reinforced?] compositions compared with traditional constructional materials are associated primarily with the possibility of a wide-scale variation of virtually all the properties of the material, which may be achieved by selecting the components and their proportions in the composition, the interaction conditions, the method of reinforcement, and other ways. Depending on the requirements which must be met by the composite materials, fibres and articles made from them, single-crystal fibres, films, hollow spheres, and other materials may be used as fillers [28].

High-strength, high-modular composite materials based on glass, boron, and carbon fibres and characterised by effective physicomechanical parameters are of special interest. The theoretical strength of steel and asbestos is 2000 and that of glass fibre is 1000 kgf mm^{-2}; on the other hand, the real strength is much lower and amounts to 250 kgf mm^{-2} for steel and 300 kgf mm^{-2} for asbestos. There is a theoretical possibility of increasing considerably the strength of articles made from polymeric materials; indeed, the strength of carbon fibres already reaches 300–400 kgf mm^{-2}. The problem of synthesising strong materials will evidently be solved also chemically, by synthesising polymers with rigid macromolecules. The ordered structure of polymers, achieved in different ways, will play a major role in this process.

Antifriction self-lubricating plastics (ASP plastics), which have found extensive applications in the construction of friction units (ball bearings, etc.) not requiring liquid lubricant, constitute a most interesting form of composite materials [31].

The problem of synthesising polymers for use in medicine with a wide variety of properties, such as thrombogenic properties, the ability to be dissipated in the organism, and conversely stability under the conditions of the living organism, pharmacological activity, etc., which are essential for the manufacture of artificial hearts, kidneys, livers, and other organs, is extremely urgent. The interesting problems of the synthesis of catalysts which are analogues of enzymes and of various biopolymer-like materials are also attracting the attention of investigators.

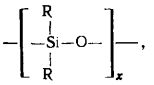
Increasing attention is being devoted to the problem of stereoregulation in the synthesis of polymers. In the field of polymerisation this involves the synthesis of stereoregular (isotactic, etc.) polymers, the synthesis of optically active polymers, the preparation of *cis*-1,4- and *trans*-1,4-polydienes, and the synthesis of stereoblock polymers. In the field of polycondensation examples of the regulation of the structure in the course of synthesis are provided by acceptor-catalytic polycondensation, the preparation of globular or fibrillar structures in polyarylates as a function of the conditions of synthesis, and the formation of right-handed or left-handed helices in polypeptides.

The study of copolymerisation and copolycondensation in order to obtain copolymers of practical value is being vigorously prosecuted [32]. Graft and block copolymerisation, which lead to new procedures for modifying polymers in a wide variety of ways, have developed greatly. Block copolymers, including polycondensation block copolymers, make it possible to obtain new types of elastomers, which do not require vulcanisation, as well as polymer systems suitable for the preparation of membranes capable of selective separation of gaseous mixtures.

Exceptionally important prospects have arisen in connection with the "chemical moulding" of polymers, which make it possible to obtain finished articles in the course of synthesis, for example, the manufacture of sheet poly(methyl methacrylate). Polyamides in the form of films or fibres can be obtained by interfacial polycondensation.

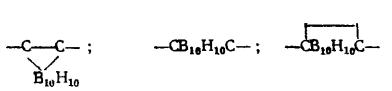
Anionic polymerisation of ϵ-caprolactam, which makes it possible to obtain poly-ϵ-caproamide in the form of finished articles of any shape which do not require mechanical working ("caprolite"), is of very great interest [33]. There is not doubt that the "chemical moulding" of polymers in the course of synthesis constitutes one of the most advanced procedures whereby one can eliminate the laborious processing steps usually employed when powdered polymers are used. In this case synthetic chemists merely copy nature, which learned a long time ago to synthesise silk, cotton, and other fibres from monomers, to form the skin of animals, blood vessels, etc.[17] There is no doubt that the polymer technology of the future will be largely based on chemical moulding processes.

The chemistry of organoelemental compounds, whose foundations were laid by A. N. Nesmeyanov, has itself become the foundation on which the edifice of the chemistry of organoelemental polymers grew [34]. K. A. Andrianov, who discovered the ability of silicon to form chains of alternating silicon and oxygen atoms, has played an outstanding role in the creation and development of the new field of the chemistry of polymers with inorganic main molecular chains. These polymers, having the structure



and known as polysiloxanes, have found an honourable place in polymer science and industry [35]. Despite the close relation between carbon and silicon, these polymers proved to constitute a completely unusual and very interesting group. Further studies showed that each element in the macromolecule makes its contribution to the set of properties of the polymer.

Polycarboranes are a very interesting group of polymers characterised by an unusual set of properties [36]. Together with various organic groups, their macromolecules contain *o*-, *m*-, or *p*-carborane rings:



Phosphorus-containing polymers, such as polyphosphazines having the structure [35]

$$-[N=P(R_2)]_x-$$

are also a promising group.

Table 1. Chemical elements in the composition of known polymers.

Period	Group of elements							
	I	II	III	IV	V	VI	VII	VIII
1							H(D)	
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	—	Ti	V	Cr	Mn	Fe Co Ni
	Cu	Zn	Ga	Ge	As	Se	Br	
5	—	Sr	—	Zr	Nb	Mo	—	Ru Rh Pd
	Ag	Cd	—	Sn	Sb	Te	I	
6	—	Ba	Ce	Hf	Ta	W	—	Os Ir Pt
	Au	Hg	Tl	Pb	Bi	—	—	
7	—	—	—	Th	—	U	—	

Table 2. Distribution of papers on methods of synthesis.

Method	Proportion of papers,%
Polymerisation	51.4
Polycondensation	27.1
Modification	21.5

Table 3. Distribution of papers on the synthesis of new polymers.

Method	Proportion of papers devoted to the synthesis of new polymers in terms of methods of synthesis, %	Proportion of papers devoted to the synthesis of new polymers, % of total number of papers on given method of synthesis
Polymerisation	38.9	27.7
Polycondensation	49.3	66.6
Modification	11.8	20.0

The task of finding ways of synthesising a wide range of polymers, incorporating the entire wide variety of the elements in the Periodic System, is of great importance [35]. Thus the polymeric structures known at the present time include 59 elements in Mendeleev's Table, as shown in Table 1. [37]

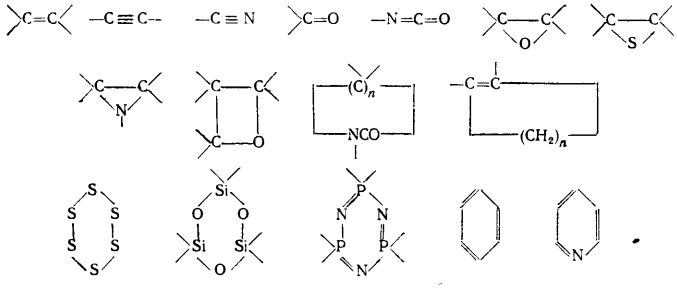
We shall consider the importance of methods of synthesis of polymers such as polymerisation, polycondensation, and modification of existing polymers. Among the chemical papers published in 1974 in the journal "Vysokomolekulyarnye Soedineniya" (Macromolecular Compounds), 89.4% were devoted to the synthesis of polymers; their distribution with respect to methods of synthesis was as shown in Table 2. The proportion of the total number of chemical papers describing the synthesis of new polymers was 32.8%. Table 3 shows how these papers are distributed with respect to methods of synthesis.

These data permit the conclusion that at the present stage studies on polymerisation are devoted mainly to the improvement of polymerisation methods, to the search for more active catalysts, and to the determination of the optimum conditions for the synthesis of polymers which are already known. Polycondensation studies involve the synthesis of new polymers to a greater extent than the improvement of synthetic reactions. The research in the field of modification, like that in the field of polymerisation, is also mainly directed to the study of chemical reactions of polymers and the improvement of modification reactions. We shall next consider the state of affairs in each of these fields of the synthesis of polymers.

V. POLYMERISATION

In considering the syntheses of polymers, one should note that a characteristic feature of polymerisation is the presence of many structures of new monomers and of many new polymerisation processes.

The range of active functional groups used to prepare polymers has been greatly extended. The most important of these, used in polymerisation, are indicated below:



Polymerisation processes, occurring as reactions involving additions to double bonds and rings, are being vigorously investigated at the present time and considerable advances may be noted in this field.

Table 4 presents the polymerisation processes known at the present time and the dates of their discovery.

A characteristic feature of the modern period is the vigorous development of research into polymerisation processes. Together with the considerable progress in the development of classical methods such as radical, cationic, and anionic polymerisation of unsaturated compounds as well as the polymerisation of heterocycles, new polymerisation processes have been discovered and investigated in detail. Among these we shall mention in the first place ionic-coordination polymerisation, migration polymerisation, polycyclotrimerisation, polydisproportionation, Diels–Alder polymerisation, 1,3-dipolar polyaddition, etc. Ziegler's discovery [50] in 1950 of catalysts for the low-pressure polymerisation of ethylene initiated the period of rapid progress in the polymerisation of olefins and other monomers. In a series of brilliant investigations by Italian scientists, Natta [46] discovered a new pathway to the development of stereospecific polymerisation processes.

Stereospecific polymerisation has become the leading field in polymer synthesis, in which many scientists of all countries are engaged. These investigations led to the

industrial manufacture of many polyolefins: polyethylene, polypropylene, ethylene–propene copolymers, many higher polyolefins, poly(*cis*-1,4-polybutadiene) and poly-(*cis*-1,4-isoprene)—new types of synthetic rubbers which are complete substitutes of natural rubber, etc. As a result of studies by S.V.Lebedev, B.A.Dolgoplosk, A.A.Korotkov, and others, our country now occupies a leading place in the world as regards the technical quality and range of synthetic rubbers.

Table 4. Polymerisation processes.

Reaction	Year of discovery	References
Radical polymerisation	1839	38
Cationic polymerisation	1873	39
Anionic polymerisation	1878	40
Diels–Alder polymerisation	1926	41
Migration polymerisation	1937	42
Hydrolytic polymerisation of heterocycles	1938	43
Cyclopolymerisation	1949	44
Dehydropolymerisation	1951	45
Stereospecific polymerisation	1955	46
Onium polymerisation	1961	47
1,3-Dipolar polyaddition	1963	48
Polycyclotrimerisation of acetylenic compounds	1965	49
Polydisproportionation	1967	52

Four mechanisms of chain propagation in ionic (cationic and anionic) polymerisation are now believed to be possible:

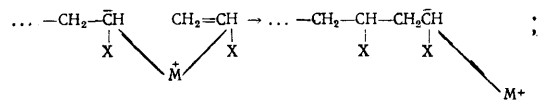
(1) polymerisation with participation of a free ion:

$$\ldots -CH_2-\overset{+}{C}HX + CH_2=CHX \rightarrow \ldots -CH_2-CHX-CH_2-\overset{+}{C}HX;$$

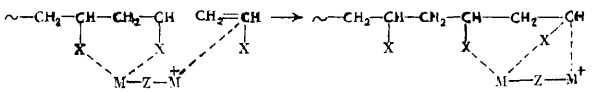
(2) polymerisation with an ion pair:

$$\ldots -CH_2-\overset{+}{C}H\ldots A^- + CH_2=CH \rightarrow \ldots -CH_2CH-CH_2\overset{+}{C}H \ldots A^-;$$

(3) two-centre coordination polymerisation:



(4) many-centre coordination polymerisation:



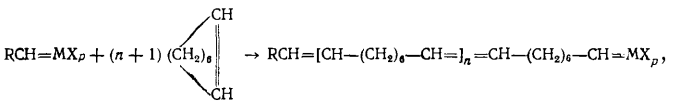
Stereoregulation is possible in each of these cases. However, in the first and second cases this possibility is realised only at low temperatures, while in the third and fourth cases the process is observed also at elevated temperatures. In the elementary chain propagation step of many-centre coordination polymerisation the polar groups of the monomer and the polar groups of the last two units of the growing chain form a complex with more than one active centre of the composite or associated catalyst, which limits the free rotation of the ends of the chains and the monomer molecules and ensures a definite disposition of the units in the elementary chain propagation step.

Isomerisation polymerisation accompanied by the isomerisation of the units has proved to be a very special case in the syntheses of polymers via both radical and particularly ionic polymerisation. This results in the formation of anomalous units and of heterochain polymers [16].

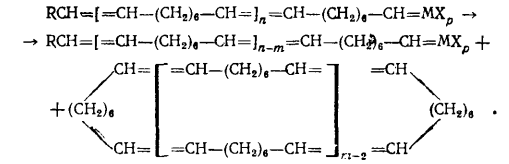
Studies on regular copolymerisation, leading to copolymers with a regular alternation of units, have been considerably developed [51]. The copolymers thus produced are frequently substances with an interesting set of properties.

A new field in polymerisation is polydisproportionation occurring in the presence of molybdenum- and tungsten-containing catalytic systems. Cyclic olefins such as cyclo-octadiene, cyclo-octene, norbornene, etc. are used as the initial monomers in this reaction [52,53].

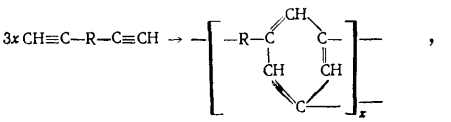
The polydisproportionation reaction proceeds in accordance with the equation

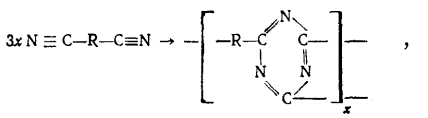


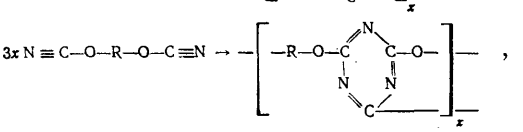
where M = Mo or W, and is accompanied by the formation of cyclic oligomers. A carbene is the intermediate active centre in this reaction, which proceeds as a chain process [54]. Cyclic oligomers are formed in this process as a result of the degradation of the active polymeric macromolecule via the reaction [55]



A new method for the synthesis of polymers with different structures, based on the cyclotrimerisation of multiple carbon–carbon and carbon–nitrogen bonds, has been developing vigorously recently. The polycyclotrimerisation of diacetylenes, dinitriles, dicyanates, and di-isocyanates, leading to the formation of benzene or triazine rings in accordance with the equations [56–58]







is particularly interesting. This reaction leads to a new way of synthesising polymers containing aromatic and heterocyclic groups in the macromolecules [59].

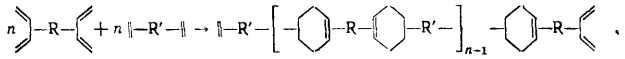
The polymerisation of aldehydes, ketones, and other carbonyl compounds has recently attracted the attention of investigators [60]. The polymerisation and copolymerisation of formaldehyde, which proceeds as a cationic process, namely

$$x\,CH_2O \rightarrow -[-CH_2-O-]_x- \quad ,$$

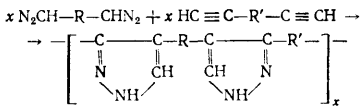
is being particularly vigorously investigated. Studies by N.S.Enikolopyan, who demonstrated the occurrence of an

unusual chain termination stage called "chain transfer with branching", have made a major contribution to the study of this process [61].

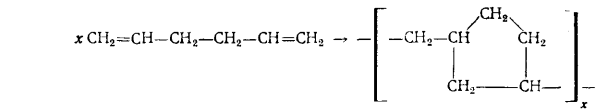
Polymers containing rings in the chain have been obtained with the aid of diene or Diels–Alder synthesis [62]. In this case it is necessary that the molecules of the initial monomer should contain a diene system and a dienophile, capable of reacting with one another under specified conditions via the mechanism



An unusual instance of polymerisation is the formation of polypyrazoles by the reaction of bisdiazo-compounds with diacetylenes via the 1,3-dipolar addition mechanism according to the equation [63]

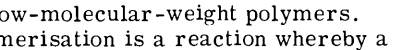


Cyclopolymerisation is a method of obtaining polymers containing cyclic groups in the macromolecular chain [44]:



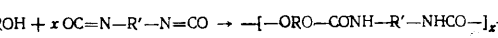
It occurs in the polymerisation of various dienes containing separated double bonds. The reaction usually yields comparatively low-molecular-weight polymers.

Dehydropolymerisation is a reaction whereby a *p*-zylylene polymer has been obtained [45]. It occurs in the formation of *p*-xylylene and is described by the following equation:

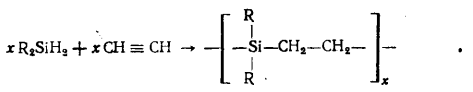


This process has also been carried out for a number of xylene analogues. The resulting biradicals are extremely reactive and readily copolymerise with other monomers.

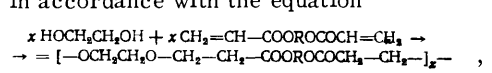
Migration polymerisation is polymerisation involving the transfer (migration) of hydrogen atoms at each stage [64]. This process is sometimes referred to as polyaddition. The polymerisation of aldehydes via the Tishchenko reaction [65], the formation of polyacetals [66], the formation of polyamides from bisoxazolones and diamines [67], and the synthesis of important polymers such as polyurethanes and polyureas by the reaction of di-isocyanates with glycols and diamines [42] are of this type. The range of these processes has been increasingly expanded recently. As examples, we may mention the formation of polyurethanes



and the synthesis of organoelemental polymers containing silicon, germanium, and tin via hydride addition [68]:

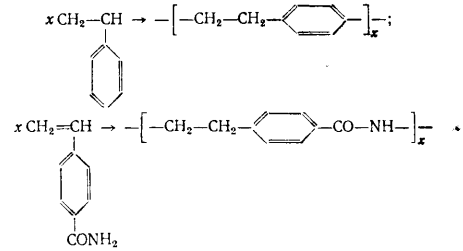


The formation of polymers via the addition of glycols or diamines to diacrylate or dimethacrylate esters, which proceeds in accordance with the equation [69]

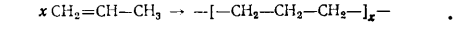


is of the same type.

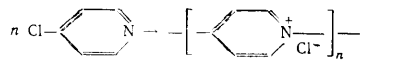
Many isomerisation polymerisation reactions also take place with migration of hydrogen [14]. Thus styrene and substituted styrenes can form polymers via the following mechanisms [70,71]:



The anionic polymerisation of propene is also accompanied by isomerisation and leads to the formation of polyethylene [72]:



Onium polymerisation has been investigated in relation to the reaction of γ-chloropyridine [47]:



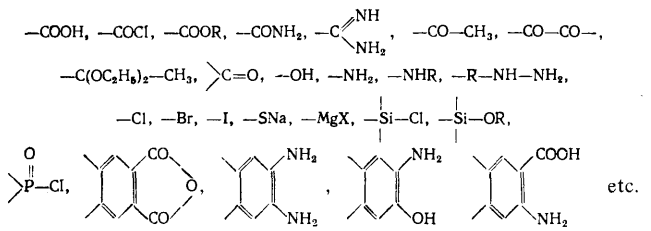
Polymerisation processes may be initiated with the aid of energetic influences such as ionising radiation, explosive impact, high pressure, mechanical action, etc. [73–75] Ionising radiation has found practical application in the initiation of polymerisation [76]. An interesting case is the initiation by this procedure of solid-state polymerisation, particularly at low temperatures [74,75].

The study of solid-state polymerisation at low temperatures enabled Semenov [77] to devise the collective interaction theory. According to Semenov, solid-state polymerisation takes place very fast when a frozen monomer is irradiated, because, as a result of a particular orientation in the crystal, the ion or radical combines not with a single monomer molecule but with a chain of molecules at once, in the region where the crystal is ideal. Thus, owing to the favourable disposition of the molecules in the crystal, there exists a kind of "seed" for the formation of macromolecules (which is not the case in liquids) and this ensures a faster polymerisation.

The polymerisation of cyclic compounds has been acquiring increasing importance as a general method for the synthesis of macromolecular compounds. Many heterochain polymers containing oxygen, nitrogen, sulphur, metals and other elements as heteroatoms have been obtained in this way. Cyclic compounds polymerise via a typical polymerisation mechanism and the process can be achieved as a stepwise (hydrolytic) polymerisation and as a chain reaction (anionic polymerisation). It is now known that all cyclic systems with sufficiently polar or polarisable bonds are capable of polymerisation regardless of their size. The polymerisation of siloxane rings, widely used as a method of synthesis of polysiloxane rubbers and other polymers, is very important [78]. Polymerisation of cyclic systems by a very rapid method, involving the use of activators, is particularly promising [79]. The use of activators in the anionic polymerisation of ϵ-caprolactam is extremely effective: it makes it possible to carry out the process over a short period at comparatively low temperatures.

VI. POLYCONDENSATION

Processes of the polycondensation type have been extensively developed in connection with the synthesis of thermostable polymer and other polymeric compounds of different types. In the first place mention should be made of the large number of monomers, containing a wide variety of functional groups, which are used in polycondensation processes, for example:



Polycondensation has been known for a long time as a general method for synthesis of polymers. It proceeds as a substitution reaction and is usually accompanied by the formation of a low-molecular-weight product [80]. Table 5 gives the dates of discovery of individual types of polycondensation.

Table 5. Polycondensation processes.

Reaction	Year of discovery	References
Equilibrium polyesterification	1833	3
Polyamidation	1862	81
Phenol-aldehyde polycondensation	1872	82
Polyazination	1889	83
Interfacial polycondensation	1898	84
Polyheterocyclisation	1908	85
Polycoordination	1953	86
Acceptor-catalytic polycondensation	1956	87
Polyrecombination	1957	88
Oxidative polycondensation	1960	89
Polycyclocondensation	1960	90
Stereospecific polycondensation	1970	91
Disproportionation polycondensation	1972	92

The study of the mechanisms of polycondensation processes made it possible to understand the laws governing their course and to devise a theory of these reactions [93,95]. The present development of polycondensation processes has led to the discovery of new polycondensation processes together with a deeper understanding of the reaction mechanism.

Depending on the structure of the starting materials and the way it is carried out, polycondensation can be achieved in two versions [94]: (1) equilibrium polycondensation; (2) non-equilibrium polycondensation. In equilibrium polycondensation the equilibrium constant of the reaction is in the range from 1 to 10^3, while in non-equilibrium polycondensation it exceeds 10^3 [93]. Equilibrium polycondensation proceeds as a rule at a low rate [95]. An example of this reaction is provided by the formation of polyamides from diamines and dicarboxylic acids in the melt.

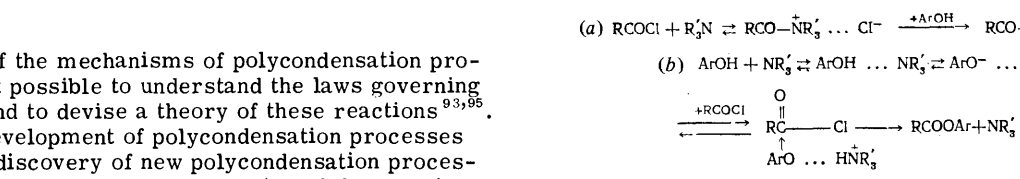
Studies on equilibrium polycondensation during the period under consideration have been characterised by a deeper understanding of the fundamental characteristics of the processes and their wide-scale application in the synthesis of many new, mainly heterochain polymers (polyamides, polyesters, polyazines, coordination polymers, etc.). Equilibrium polycondensation is based on reversible elementary equilibrium reactions [95]. A new instance of equilibrium polycondensation is disproportionation polycondensation in accordance with the equation [92,96,97]



Together with equilibrium polycondensation, there are also polycondensation processes based on irreversible elementary reactions. Reactions of this type belong to the group combined under the general name "non-equilibrium polycondensation" [93]. There is a fairly large number of instances of non-equilibrium polycondensation. They include oxidative polycondensation reactions, polyrecombination, polycyclisation, as well as interfacial polycondensation, acceptor-catalytic polycondensation, and polycyclocondensation.

Non-equilibrium polycondensation is characterised by high equilibrium constants and as a rule a high rate [6,93]. An example of reactions of this type is provided by the formation of polyamides from diamines and dicarboxylic acid chlorides. There are many instances of non-equilibrium polycondensation where the reaction is comparatively slow. However, the polymers produced by the reaction are stable under its conditions and incapable of being hydrolysed or of undergoing degradative transformations, which is the reason for the irreversibility of the overall reaction. Dehydropolycondensation, polyrecombination, and polycyclisation, which were examined below, were examples of reactions of this kind.

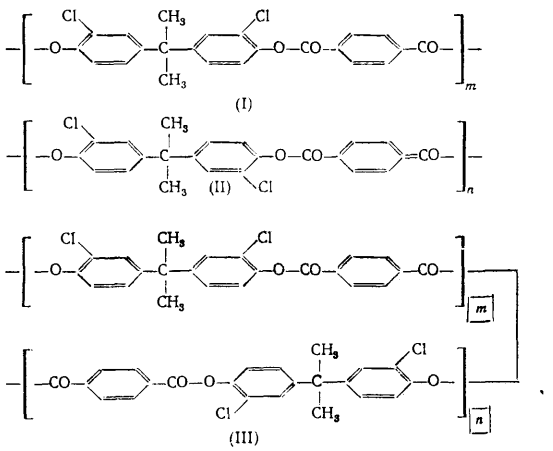
Polycondensation in solution, carried out at temperatures below 100°C, also referred to as low-temperature polycondensation, has recently attracted much attention by investigators and its various aspects are being vigorously developed. In the synthesis of polyesters from acid dihalides and diols in the presence of tertiary amines, it is referred to as acceptor-catalytic polycondensation [98]. In the synthesis of polyarylates the process proceeds via nucleophilic (a) or general base (b) catalysis in the following way:



Apart from the activities of the starting materials, the formation of macromolecules is influenced by the nature of the solvent and the tertiary amine, particularly its ability to form complexes with the starting materials. The method permits a very fine control of the structure of the polymers obtained.

Conformationally-specific polycondensation has been achieved under the conditions of acceptor-catalytic polyesterification for the reaction of 3,3'-dichlorodian with terephthalic acid chloride [91]. The reaction results in the formation of macromolecular conformers whose structure is determined by the nature of the solvent and the tertiary

amine[99,100]. The formulae of polyarylates formed by this reaction are given below:

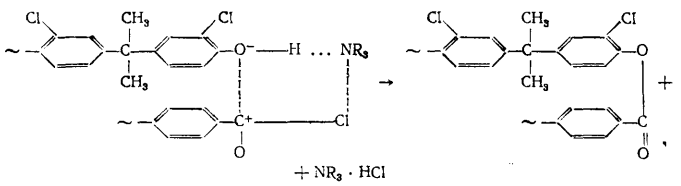


(I)

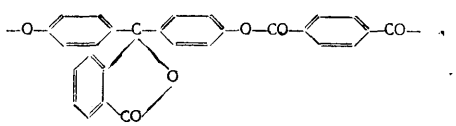
(II)

(III)

Here (I), (II), and (III) are *cis*-tactic, *trans*-tactic, and heterochain (atactic) polymers containing units of both conformations. The nature of the tertiary amine has a significant influence on the conformationally specific polycondensation, which is attributed to the formation of cyclic intermediate complexes[100]. In general base catalysis such a complex can be represented as follows:



The use of phenolphthalein and similar substances as starting materials in the reaction of an acid dichloride and a bisphenol leads to the formation of cardopolymers[101], a characteristic feature of which is that the carbon atom in the monomer residue is at the same time part of the polymer chain. The polyarylate formed from phenolphthalein and terephthalic acid is an example of such a cardo-polymer:



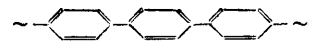
Oxidative polycondensation is being developed on an increasing scale as a general method for the synthesis of various polymers[102,103]. The application of this reaction to diacetylenic compounds of the type $HC\equiv C-R-C\equiv CH$ made it possible to obtain a large number of linear polymers having the general formula

$$-[-C\equiv C-R-C\equiv C-]-_x,$$

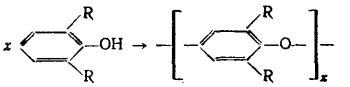
containing triple bonds in the chain together with phenyl and other groups. "Carbene", which is a linear form of carbon, has been obtained in this way from acetylene[89]. It is formed in the oxidation of acetylene in the presence of copper salts via the reaction

$$n\,HC\equiv CH \xrightarrow{Cu^{2+}} -[-C\equiv C-]_n- \quad .$$

A polyphenylene has been obtained by oxidative polycondensation from benzene[104]:



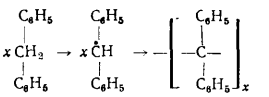
The oxidative polycondensation of 2,6-disubstituted phenols makes it possible to obtain polymeric phenyl ethers—poly(phenylene oxides):



This oxidative process takes place in the presence of catalysts (copper salts) and an oxidant[105].

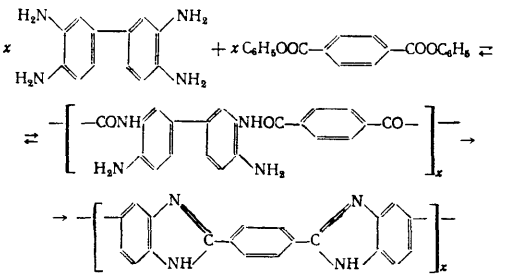
Increasing attention has been devoted recently in polymer chemistry to the problem of the synthesis of polymers with substances which are not monomers in the present sense of this term, i.e. do not contain double bonds, rings, or any other traditional functional groups. One of the ways of solving this problem is to employ a polyrecombination reaction, whereby saturated hydrocarbons and other substances incapable of polymerising in the usual way can be converted into polymers.

Polyrecombination involves the synthesis of polymers via the mechanism (when diphenylmethane is used as a starting material)[106]



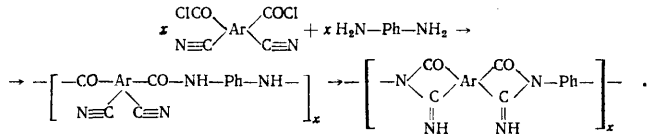
The elementary processes in polyrecombination are the formation and recombination of free radicals. A characteristic feature of the monomers used in polyrecombination is the presence of hydrogen atoms, which are easily removed by free radicals. When the monomer contains two reactive hydrogen atoms, linear polymers are obtained and in the presence of three and more atoms the products are branched and three-dimensional polymers.

Polycyclisation is a new type of reaction leading to the formation of polymers having a cyclochain structure[107]. Although in terms of its mechanism the reaction is a polycondensation process, its mechanism is in fact extremely unusual. In the first stage this involves an ordinary equilibrium reaction leading to the formation of polyamides, polyesters, polyhydrazones, and similar compounds, depending on the structure of the starting materials. The characteristics of this stage do not in general differ from those known for analogous reactions. In the second stage, cyclisation proper takes place, i.e. the closure of the heterocycle characteristic of the given reaction. This stage constitutes non-equilibrium polycondensation, since the formation of stable rings is as a rule an irreversible process, which proceeds in the case of the synthesis of polybenzimidazoles by the Marvel method in accordance with the equation[108]

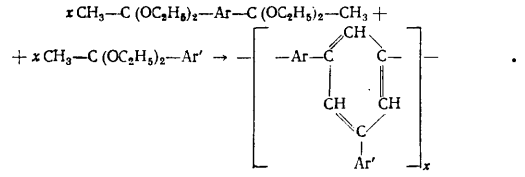


The polycyclisation reaction has been investigated nowadays in relation to the synthesis of polymers incorporating in their chains heterocycles such as thiazole, imidazole, pyrazole, triazole, oxadiazole, phthalimide, triazine, benzimidazole, benzoxazole, benzothiazole, etc.[109]

An interesting instance of polycyclisation is isomerisation polycyclisation, where the starting materials are aromatic acid dichlorides or diamines containing cyano-groups in the ring[110]. Under these conditions, the first stage involves non-equilibrium polycondensation, leading to the formation of polyamides. The latter then undergo cyclisation as a result of their addition to cyano-groups, as shown below:



Polycyclocondensation is a process involving the synthesis of polymers whose mechanism is close to that of polycyclotrimerisation[122]. Macromolecules are formed as a result of the formation of aromatic or heterocyclic units linking the molecular residues of various initial substances. As an example, one may quote the formation of polyphenylene from the diketal of *p*-diacetylbenzene and the ketal of acetophenone via the reaction



The polycondensation reactions considered above take place in the vast majority of cases as ionic processes which are extremely sensitive to the action of catalysts. The use of catalysts to accelerate the polycondensation reaction is therefore extremely effective[100].

VII. MODIFICATION OF POLYMERS

The reaction involving the modification of existing polymers has been developed on an increasing scale in the synthesis of polymers with a wide variety of structures. Whereas previously natural polymers (cellulose, starch, proteins) were subjected to modification processes, nowadays many synthetic polymers are used in this process. Table 6 presents examples and the dates of the first communications concerning the most important reactions of this type and shows that the modification reactions can be divided into three main groups: (1) chain substitution reactions; (2) structure formation reactions; (3) exchange reactions involving heterochain polymers.

Chain substitution reactions involving natural polymers (cellulose, starch, proteins, etc.) have been known for a long time and involve mainly the substitution of a hydrogen atom in a hydroxy- or amide group as well as hydrogen atoms linked to carbon in methylene or phenyl groups. These reactions have been investigated in relation to numerous examples and processes of this kind have been justified theoretically[116]. There are many side reactions as a result of which the polymers obtained are of the "heterounit" type[117]. The reactions of synthetic polymers involving the substitution of hydrogen atoms linked to carbon, halogen atoms, the sulpho-group, the phosphono-group, and alkyl-groups are of increasing importance. The introduction of polar groups such as the carboxy-, amino-, sulphonic, phosphonic, etc. substituents leads to the appearance of ion-exchange properties and is widely used in the synthesis of ion exchangers. Investigations of the grafting of carbochains and heterochain polymers on to cellulose have been greatly developed. Rogovin[118] showed that this makes it possible to modify extensively the properties of cotton and other cellulose materials. The structure of formation reactions discovered for natural polymers are being used on an increasing scale for synthetic polymers. Examples of this kind are provided by the radiation-induced vulcanisation of polyethylene and other polymers. As a result of these reactions, the structure of the macromolecules changes significantly.

Table 6. Modification processes.

Reaction	Year of discovery	Refs.
Nitration of cellulose	1833	4
Vulcanisation of rubber with sulphur	1839	111
Grafting via chain transfer	1933	112
Chlorination of poly(vinyl chloride)	1933	113
Polyester exchange reactions	1942	114
Sulphochlorination of polyethylene	1946	115

The exchange reactions of heterochain polymers constitute a specific means of synthesising copolymers by the interaction of two different polymers on heating or in the presence of catalysts. For example, a mixed polyamide is obtained from a mixture of two polyamides[119], a mixture of a polyamide and a polyester gives rise to a polyamido-ester[120], and a mixture of two polysulphides gives rise to the corresponding copolymer[121]. Polyacetals of the type of polyformaldehyde also form copolymers in the presence of catalysts[61].

In conclusion one should note that, as can be seen from the examples presented, in the field of the synthesis of polymers there has been a continuous and notable progress. New reactions leading to the synthesis of polymers are being discovered and investigated and the synthetic processes already known are being improved. Here one should note an increasing application of catalysis to polymerisation, polycondensation, and polymer modification reactions. As a result of this, science has become enriched in a large number of new polymers and many previously known polymers obtained by new improved methods have acquired a set of more valuable properties. A characteristic feature of the synthetic branch of the development of polymer chemistry is more detailed study of increasingly more complex chemical reactions, used in polymer synthesis, and the preparation of new extremely complex polymer structures, which characterises the growth of the chemical art in polymer synthesis and an extensive application of modern physical research techniques. Finally, one should note that a particularly characteristic feature of modern polymer synthesis is the endeavour to obtain polymers not only for constructional purposes, which has been characteristic of the earlier period of the development of polymer science, but to an

increasing degree to synthesise polymers with a specific set of chemical and physical properties. As an example, we may point to thermostable, non-combustible, semiconducting, electrically conducting, photoelectrically active, light sensitive, and biologically active polymers, polymers resembling biopolymers, polymeric catalysts, ion exchangers, complexones, and other polymers with a wide spectrum of specific properties.

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Advances in Acceptor-catalytic Polyesterification

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Advances in the synthesis of polymers and copolymers by acceptor-catalytic polyesterification from dicarboxylic acid dichlorides and diols in the presence of tertiary amines are examined. The considerable possibilities of this method are demonstrated. It makes it possible to obtain polymers and copolymers of different composition and structure, including stereoregular polycondensation polymers of a new type—conformationally-regular polyarylates. The study of acceptor-catalytic polyesterification made it possible to establish experimentally the principal characteristics of the formation of polymers containing "head-to-tail" fragments and of copolymers under the conditions of non-equilibrium polycondensation and copolycondensation in a homogeneous system. The bibliography includes 128 references.

CONTENTS

I. Introduction 16
II. Synthesis of polyesters by acceptor-catalytic polyesterification 16
III. The kinetics, mechanism, and characteristics of acceptor-catalytic polyesterification 17
IV. Characteristics of the synthesis of copolymers in a homogeneous system 21
V. Characteristics of the synthesis of polyesters from diols with an asymmetric distribution of hydroxy-groups 22
VI. Synthesis of conformationally regular polyarylates 23

I. INTRODUCTION

As a method of synthesis of polymers, polycondensation was discovered in the past century. Many different polycondensation processes, based on particular substitution reactions, are now known. All these processes can be divided into two types: equilibrium (reversible) and non-equilibrium (irreversible) polycondensation[1].

Analysis and survey of a large number of experimental data made it possible to discover the fundamental features and general characteristics of equilibrium polycondensation[2]. In contrast to equilibrium polycondensation, which has been thoroughly investigated, non-equilibrium polycondensation had been scarcely studied by the 1960s[3]. However, at that time it had already been established that non-equilibrium polycondensation has many useful features, which promoted its subsequent rapid and wide-scale utilisation in laboratory and industrial practice. These features of non-equilibrium polycondensation include the absence of exchange and degradative reactions, high polymer chain propagation rate constants, and many others. Nevertheless many problems of non-equilibrium polycondensation, largely of a fundamental type, have until recently either not been considered at all or have been only slightly touched upon in a few publications. Such exceptionally important problems include those of the kinetics, mechanism, and fundamental characteristics of the formation of macromolecules of homogeneous and mixed polymers, including polymers with different three-dimensional microstructures and containing fragments of the "head-to-tail" type in the macromolecules[3].

Studies on the non-equilibrium polyesterification of dicarboxylic acid dihalides with diols in the presence of tertiary amines [see Eqn. (1)], known previously in the literature as "low-temperature polycondensation in solution"[3], were undertaken to solve these problems:

$$\begin{aligned} &\mathrm{HalOC{-}R'{-}COHal + HO{-}R''{-}OH + 2R_3N \rightarrow} \\ &\rightarrow \mathrm{-[-OC{-}R'{-}COO{-}R''{-}O-]_n- + 2R_3N \cdot HHal}\ , \end{aligned} \qquad (1)$$

The study of the mechanism of this reaction established that the tertiary amine plays the role of a reaction catalyst and not merely of a hydrogen halide acceptor. This justified the use of the term acceptor-catalytic polyesterification for this type of polyesterification[3,4].

In the first studies on the synthesis of polyesters by acceptor-catalytic polyesterification it was already shown that this variety of non-equilibrium polycondensation constitutes an extremely convenient method of obtaining polymers which are formed in solution at low temperatures, usually close to 20°C, the reaction terminating over a short period, as a rule within the limits of 30 min. The same factor makes acceptor-catalytic polyesterification a suitable model for the investigation of many fundamental problems associated with the characteristics of the formation of macromolecules under the conditions of non-equilibrium polycondensation.

II. SYNTHESIS OF POLYESTERS BY ACCEPTOR-CATALYTIC POLYESTERIFICATION

As a method of synthesis of polyesters (in the given case, polycarbonates), acceptor-catalytic polyesterification was used for the first time by Einhorn[5] as early as 1898. However, subsequently interest in this procedure lapsed for a long time. Only now, more than fifty years later, have chemists returned to acceptor-catalytic polyesterification[6]. During the 1950s, a vigorous development of acceptor-catalytic polyesterification began on the use of this method for the synthesis of polycarbonates from phosgene and bisphenols in pyridine or mixtures of pyridine and other organic solvents[7,8]. Many carbonates based on bisphenols of different structure have now been synthesised by acceptor-catalytic polyesterification[3,8-10].

In 1961 Sokolov and coworkers[11] synthesised polyarylates from oxalyl chloride or di(hydroxyphenyl)propane in the presence of pyridine. Morgan and coworkers[12,13] obtained polyarylates based on different dicarboxylic acid dichlorides and bisphenols by acceptor-catalytic polyesterification in the presence of tri-ethylamine. By 1965, only about ten papers had been published on the synthesis of polyesters from dicarboxylic acid dihalides and diols in the presence of tertiary amines[11-18]. This enabled Morgan[10] (p.329) to write in 1965, that, with the exception

of polycarbonates, low-temperature polyesterification "has been scarcely used for the synthesis... of polymers".

In recent years acceptor-catalytic polyesterification has begun to be used much more frequently for the synthesis of polyesters, in the first place polyarylates. The studies of Korshak and coworkers made a large contribution to the development of the synthetic possibilities of this method.

Korshak and coworkers[19,24] synthesised a large number of cardo-polyarylates [or 'cross-planar polyarylates' (Ed. of Translation)] based on 9,9-bis-(4-hydroxyphenyl)-10-anthrone and other bisphenols with cardo-groups by acceptor-catalytic polyesterification in the presence of triethylamine. Korshak and coworkers[25] synthesised by the same method cardo-polyarylates based on polycyclic bisphenols such as, for example, bis-(4-hydroxyphenyl)-2-norbornylidene. Morgan[26] reported the properties of many cardo-polyarylates, some of which could be obtained by acceptor-catalytic polyesterification in the presence of triethylamine.

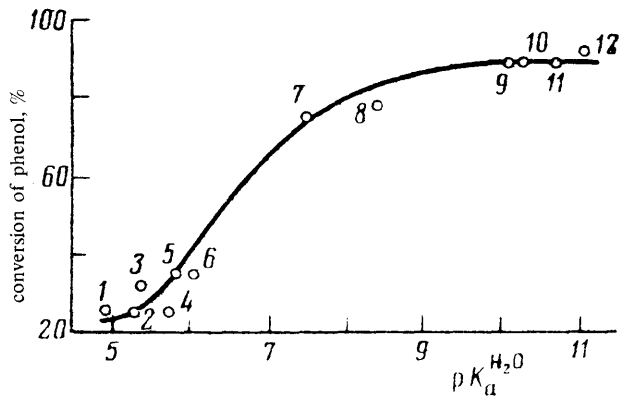


Figure 1. Dependence of the degree of conversion of phenol into phenyl benzoate on the basicity of tertiary amines. Molar ratios of phenol, methanol, tertiary amine, and benzoyl chloride 2.5 : 2.5 : 1 : 1, (dichloroethane, 25 °C)[68]; tertiary amines: 1) quinoline; 2) pyridine; 3) isoquinoline; 4) β-picoline; 5) quinaldine; 6) α-picoline; 7) γ-collidine; 8) triallylamine; 9) ethyldimethylamine; 10) cyclohexyldimethylamine; 11) triethylamine; 12) tributylamine.

Numerous communications have been published during the last decade on the synthesis of many polyesters with a wide variety of structures from dicarboxylic acid dichlorides and diols in the presence of tertiary amines[27-36]. Among these, mention should be made of the work of Jedlinski and coworkers[30,31] on the synthesis of interesting, as regards practical applications, polyesters with naphthalene rings in the chain. Korshak and coworkers[33] were the first to obtain by acceptor-catalytic polyesterification polyesters based on bis-β-dicarbonyl compounds reacting in the enolic form.

Acceptor-catalytic polyesterification became very important as a method of synthesis of organoelemental polymers, particularly carborane-containing polyesters[37]. Thus Korshak and coworkers[37-46] were the first to obtain polyarylates with *o*- and *m*-carborane groups in the chain from the dichlorides of 1,2- or 1,7-bis-(4-carboxyphenyl)-carboranes and 1,2-bis-(4-hydroxyphenyl)carborane in the presence of triethylamine. They[37,47-50] used acceptor-catalytic polyesterification for the synthesis of carborane-containing polyesters and copolyesters from the dichlorides of *m*- or *p*-carboranedicarboxylic acids. Soluble and fusible polyester-chelates have also been obtained by acceptor-catalytic polyesterification[51]. Bisphenols, containing copper chelates, for example, bis(acetoacetatohydroquinone)copper, were used for this purpose in the reaction with the dichloride of diphenylphthalide-4,4'-dicarboxylic acid.

Thus studies in this field have now established the considerable synthetic possibilities of acceptor-catalytic polyesterification, whereby polyesters have been obtained with a wide variety of structures and possessing in many instances a set of interesting properties. It appears particularly promising to use this method for the synthesis of polymers which are extremely valuable in practice, namely polyarylates, including polycarbonates.

The problems of the synthesis of mixed polyesters, polyesters based on diols with an asymmetric distribution of hydroxy-groups ("head-to-tail"), and conformationally regular polyarylates by acceptor-catalytic polycondensation are examined in subsequent sections of this review.

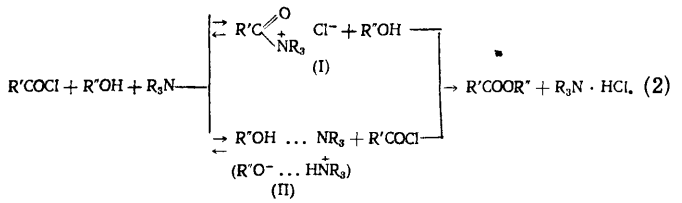
III. THE KINETICS, MECHANISM, AND CHARACTERISTICS OF ACCEPTOR-CATALYTIC POLYESTERIFICATION

Acceptor-catalytic polyesterification is one of the first examples of non-equilibrium polycondensation whose kinetics, mechanism, and principal characteristics have been studied in detail. One of the important results of such research has been the conclusion that the tertiary amine plays a catalytic role in the given reaction. The importance of this conclusion becomes understandable if one takes into account the fact that in 1959 Conix[14] attributed to tertiary amines merely the function of acceptors of the hydrogen halide evolved. Ten years later, in 1969, Billmeyer and Eckard[52] still assumed that tertiary amines behave as acceptors of the acid in the polycondensation of dicarboxylic acid dichlorides with diols, "displacing the equilibrium towards the formation of polyesters".

By 1965 there was virtually no information in the literature about the kinetics of acceptor-catalytic esterification and polyesterification. Nevertheless in his monograph Morgan[10] admitted the possibility of three different reactions under the conditions of acceptor-catalytic polyesterification: the formation of a complex of the tertiary amine and the acid chloride (nucleophilic catalysis), the formation of a complex of the tertiary amine and the phenol (general base catalysis), and simple binding of hydrogen chloride. The majority of investigators concerned with the problems of acylation and polyacylation in the presence of tertiary amines gave preference to the first of the above pathways[8,53,54].

From 1969, Korshak and coworkers[55] began systematic studies on the mechanism of acceptor-catalytic esterification and polyesterification. They established by ^{35}Cl NQR and potentiometric measurements that the interaction of tertiary amines with carboxylic acid chlorides involves the formation of ionic complexes of the type of acylammonium salts (I) [see Eqn. (2)]. The equilibrium complex-formation constant is appreciably influenced by the steric

and resonance factors, while the basicity of the tertiary amine plays a secondary role[56,57]:



At the same time it was found by ^{1}H NMR and infrared spectroscopy that, under conditions close to those in acceptor-catalytic polyesterification, tertiary amines form hydrogen-bonded complexes (II) with phenols [see Eqn. (2)], whose stability increases with increasing acidity of the donor and basicity of the acceptor[58-60]. In many instances it was possible to isolate and investigate the equimolar complexes of bisphenols with trialkylamines[60-62].

Bearing in mind the virtual irreversibility of the reactions of carboxylic acid chlorides with phenols[63,64], the mechanism of acceptor-catalytic polyesterification can be represented on the basis of the results of studies of the initial stages of the reaction[55] by two catalytic fluxes: a nucleophilic flux [the formation of complex (I)] and the general base-catalytic flux [the formation of complex (II)]. The study of the esterification kinetics[65-67] and determination of the relative activities of the starting compounds by the competitive acylation method[68,69] established that, in the absence of steric hindrance at the reaction centre, an increase of the acidity of the hydroxylated compound and of the basicity of the tertiary amine creates conditions for reaction via the general base catalysis. Thus it was found for the competitive benzoylation of phenol and methanol that, in the presence of triethylamine, the degree of conversion of the more acid reagent (phenol) greatly exceeds that of the less acid reagent (methanol) (Fig. 1). This shows that the general base catalysis predominates under the given conditions over nucleophilic catalysis. On the other hand, if the competitive benzoylation is carried out in the presence of a less basic tertiary amine (pyridine), then methanol mainly reacts, i.e. nucleophilic catalysis predominates under these conditions[68].

The kinetic study showed that acceptor-catalytic esterification is of third order overall (of first order with respect to each reactant) and that the rate-limiting stage is the interaction of complex (I) with phenol or of complex (II) with the acid chloride[65-67]. It was found that the rate of benzoylation in the presence of triethylamine (in dioxan at 30°C) is greatly influenced by the acidity of phenols and the plot of the logarithm of the reaction rate constant against pK_a^{DMSO} for phenols (Fig. 2) consists of two linear sections with opposite slopes: $\lg k_3 = -0.40\ pK_a + 4.88$ ($r = 0.996$, $s = 0.05$) for phenols with $pK_a < 14$ and $\lg k_3 = 0.39\ pK_a + 5.99$ ($r = 0.973$, $s = 0.05$) for phenols with $pK_a > 14$. This permitted the conclusion that nucleophilic catalysis is possible when the following conditions are observed: (1) the tertiary amine is more basic than the leaving group in R'COX; (2) the R"–OH nucleophile attacking the acylammonium complex is more basic than the leaving ammonium ion[67]. In the system investigated the first condition is completely fulfilled, while the second apparently holds only for more basic phenols with $pK_a > 14$. For more acidic phenols ($pK_a < 14$), the second condition does not hold and the reaction proceeds via the general base catalysis pathway.

The study of the kinetics of the benzoylation of alcohols in the presence of tertiary amines in a non-polar medium led Bogatkov et al.[70] to the conclusion that, regardless of the formation of complex (I) or (II), the reaction proceeds in this case via a transition state with a five-coordinated carbon atom.

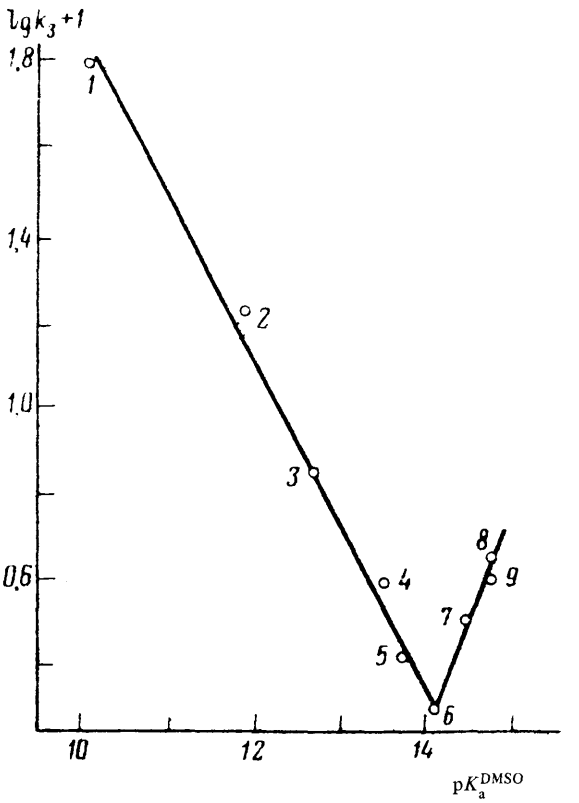


Figure 2. Dependence of the logarithm of the benzoylation rate constant on the acidity of phenols[67]; phenols: 1) *p*-nitrophenol; 2) *p*-acetylphenol; 3) *p*-chlorophenol; 4) *o*-hydroxyphenyl benzoate; 5) phenol; 6) *p*-t-butylphenol; 7) *p*-cresol; 8) *p*-methoxyphenol; 9) hydroquinone.

The solvent and reaction temperature have a marked influence on the rate of acceptor-catalytic esterification[71]. It has been found that an increase of the polarity of the solvent promotes an increase of the rate of reaction. A complex non-Arrhenius temperature dependence of the esterification rate constant (Fig. 3, curve *1*) has been established over a wide temperature range (from −30° to 80°C). The failure of the rate constant to obey the Arrhenius relation was attributed by the authors[71] to the fact that, in a complex reaction of this type, consisting of a series of consecutive stages [Eqn. (2)], temperature can have different effects on the rate of each individual stage. The resulting influence of temperature on the effective rate constant consists of these "partial" influences.

The results of the study of the kinetics and mechanism of acceptor-catalytic esterification enabled Korshak and coworkers to investigate at a qualitatively new level and to interpret the fundamental characteristics of acceptor-catalytic polyesterification as a characteristic example of non-equilibrium polycondensation[57,72]. Only a few aspects of this problem had been examined earlier[11,13,73,74]. In the analysis of the characteristics of acceptor-catalytic polyesterification and copolyesterification, data for the reactivities of diols and dicarboxylic acid dichlorides, first obtained in systematic studies of the above monomers by quantum-chemical[75,76], physical (potentiometry[77,78], ^{1}H NMR,[57,78] ^{35}Cl NQR [79,80]), and kinetic[80-83] methods, were used on a wide scale. It was established that the difference between the activities of the first and second functional groups of the monomer is determined by the distance between them, the structure of the bridge unit, and the structure of the attacking agent. Depending on the above factors, the activity of the second functional group of the monomer can decrease, remain unchanged, or after the first group has reacted, increase.

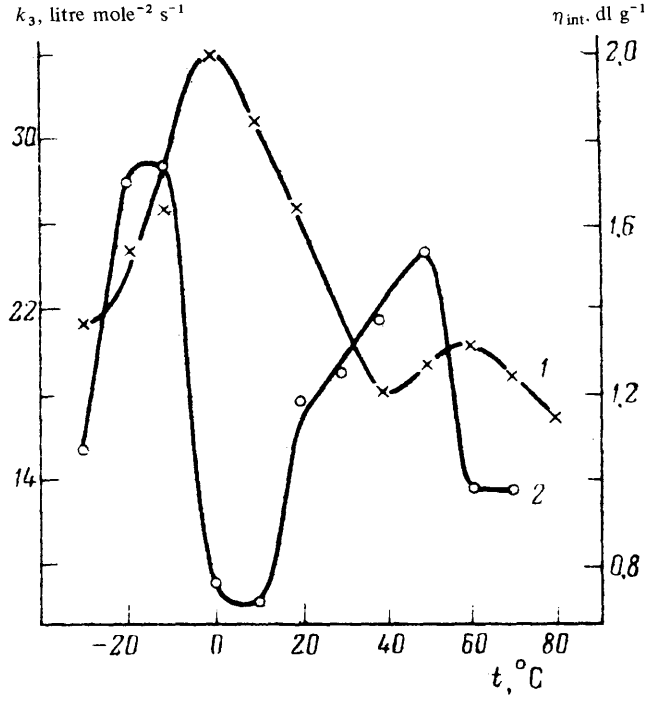


Figure 3. Dependence of the rate constant for the reaction of *o*-chlorophenol with *p*-chlorobenzoyl chloride (curve *1*) and of the intrinsic viscosity of the polyarylate obtained from 2,2-di-(3-chloro-4-hydroxyphenyl)propane and terephthalic acid dichloride (curve *2*) on the reaction temperature (toluene, triethylamine)[71].

Thus the results of the kinetic study of acceptor-catalytic esterification of terephthalic acid dichloride by phenols showed that the rate constants for the first and second COCl groups depend appreciably on the structure of the phenol (Table 1). Enhancement of the electron-accepting nature of the substituent in the phenol molecule increases the reactivity of the second COCl group of the acid dichloride, which actually begins to exceed that of the first COCl group when R = NO_2.[83] In the acceptor-catalytic esterification of di-(4-hydroxyphenyl) ether and 2,2-di-(4-hydroxyphenyl)propane by the chlorides of *p*-substituted benzoic acids, the ratios of the rate constants for the first and second OH groups have virtually the same value, which is independent of the structure of the acylating agent[83].

Table 1. Results of the kinetic study of the reaction of terephthalic acid dichloride with phenols (R–⟨⟩–OH) in the presence of triethylamine*[83].

R	k^1, litre^2 mole^{-2} s^{-1}	k^2, litre^2 mole^{-2} s^{-1}	$\varkappa = k^1/k^2$
CH_3	11.5±1.0	4.7±0.3	2.45
H	10.0±1.0	6.8±0.8	1.47
Cl	17±1	15±1	1.13
NO_2	48±2	62±3	0.77

* Here $\overline{k^1}$ and $\overline{k^2}$ are the rate constants for the reactions of phenols with the first and second COCl groups of the dichloride in dioxan at 30°C.

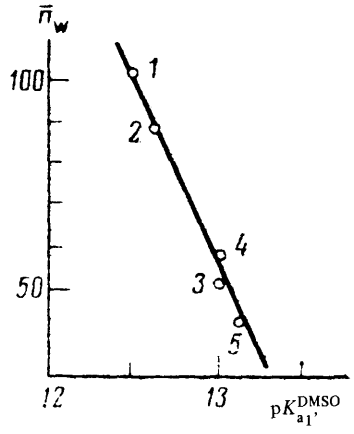


Figure 4. Dependence of the polymerisation coefficients of polyterephthalates $\bar{n}_W$ on the pK_{a_1} of bisphenols[88]; bisphenols: 1) 2,2-di-(3-chloro-4-hydroxyphenyl)propane; 2) 3,3-di-(4-hydroxyphenyl)phthalide; 3) di-(4-hydroxyphenyl)methylphenylmethane; 4) di-(4-hydroxyphenyl)-phenylmethane; 5) 9,9-di-(4-hydroxyphenyl)fluorene.

The study of acceptor-catalytic polyesterification showed that polyesters with the highest molecular weights are formed in high yields for an equimolar ratio of the acid dichloride and diol[57,84]. On the other hand, the optimum amount of tertiary amine is determined by the structure of the initial reactants. Thus, on passing from bisphenols to glycols and with decrease of the basicity of the tertiary

amine, the molar ratio of the acceptor-catalyst and the diol increases from 2 : 1 to 8 : 1.[4,57]

Comparison of the molecular weights of the polymers with the structures of the initial compounds established that, with increase of the acidity (activity) of the bisphenols[55,85,86] (Fig. 4) and the basicity of tertiary amines[87], the molecular weights of the polyarylates increase. The increase of the activity of the acid dichlorides also leads in most instances to an increase of the molecular weight of the polyarylates formed (Fig. 5); however, the increase of the activity of certain acid dichlorides is accompanied by a decrease of the molecular weight of the polymers[85,88].

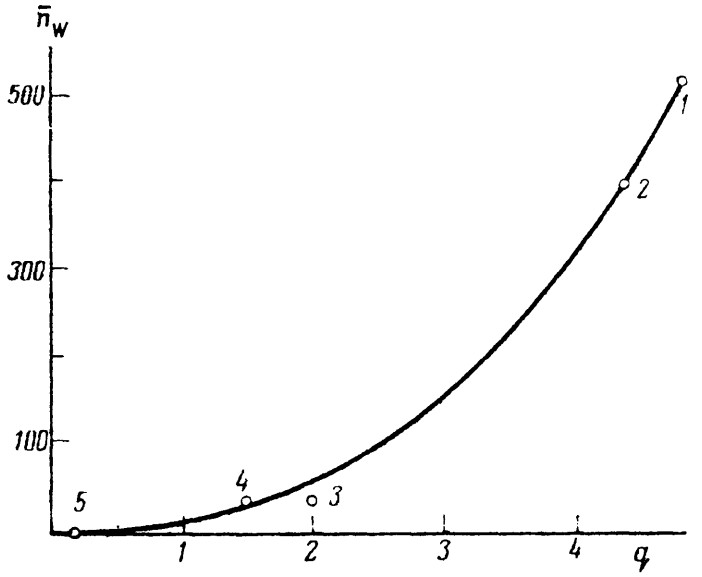


Figure 5. Dependence of the polymerisation coefficients of the polyarylates of 2,2-di-(3-chloro-4-hydroxyphenyl)-propane on the relative activity q of the acid dichloride[88]; dichlorides of different acids: 1) terephthalic; 2) isophthalic; 3) biphenyl-4,4'-dicarboxylic; 4) 1,1'-oxybisbenzene-4,4'-dicarboxylic; 5) tetrachloroterephthalic.

The study of the side reactions accompanying acceptor-catalytic polyesterification showed that the main chain-termination reactions under the conditions examined are hydrolysis and aminolysis of the acid halide groups[88,89], the contribution of these reactions increasing appreciably on passing from strongly basic (general base catalysis) to weakly basic (nucleophilic catalysis) tertiary amines[88]. Thus it has been found that in the presence of triethylamine the reactivity of diethylamine in the reaction with benzoyl chloride exceeds by several orders of magnitude the activity of phenol (Table 2). At the same time, the activity of water under analogous conditions is appreciably inferior to that of phenol. On passing to a less basic tertiary amine (pyridine), the reactivity of water increases and actually begins to exceed that of phenol (Table 2). In the presence of pyridine the role of the chain termination reaction due to the admixture of secondary amines also becomes more marked[88].

These results enabled Korshak and coworkers[88] to demonstrate experimentally for the first time that the molecular weights of the polymers obtained in non-equilibrium polycondensation depend on the ratio of the rates of chain propagation and termination. If an increase of the activity of the monomers (for example, the bisphenols) entails an increase of the contribution of the chain propagation reaction, then the molecular weight of the polymers increases. On the other hand, when an increase of the activity of the monomers (for example, acid dichlorides) is accompanied by an increase of the contribution of the chain termination reaction, the molecular weight of the polymers diminishes.

Table 2. The activities of HO- and NH_2-containing compounds relative to the activity of phenol in the reaction with benzoyl chloride in dichloroethane at 25 °C.[88]

RXH	$k_{RXH}/k_{C_6H_5OH}$ **	
	$N(C_2H_5)_3$	NC_5H_5
H_2O*	<0.1	3.4
CH_3OH	0.17	9.5
$C_6H_4NH_2$	3.0	<100
$(C_2H_5)_2NH$	>100	***

*Acylation carried out in dioxan.

**$k_{RXH}/k_{C_6H_5OH}$ is the ratio of the rate constants for the benzoylation of RXH and phenol.

***Too high for determination by the method of competitive acylation.

On the basis of the theory of the heterounit structure of polymers developed by Korshak[90], one must suppose that the occurrence of certain types of reactions leads to the formation of heterounit polyesters. Thus, when acceptor-catalytic polyesterification is carried out in the presence of moisture, there is a possibility of the appearance of anhydride linkages in the macromolecules[33,89].

Interesting data were obtained in the study of the influence of reaction temperature on the results of acceptor-catalytic polyesterification[4,55,91-95]. It was found that, in the presence of highly reactive starting compounds in a homogeneous system, the dependence of the molecular weights of polyesters on the reaction temperature is represented by curves with two maxima (Fig. 3, curve 2). The results of kinetic studies suggested that this dependence is due to the presence of more than one extremum in the relation between the rate constant for the preparation of the polymer chain and the reaction temperature[71].

The study of the influence of the concentration of the initial compounds on the molecular weight of the polyester showed that, for a fairly high activity of the functional groups, the dependence of the molecular weights of the polymers on the concentration of the monomers is represented by a curve with a single maximum at 0.15–0.2 M.[4,91-95] The low activity of at least one of the initial compounds increases the optimum concentration of monomers to 1–2 M.[4]

The nature of the solvent has a major influence on the results of acceptor-catalytic polyesterification. Korshak and coworkers[94] showed that there is a tendency towards a decrease of the molecular weight of the polyester with

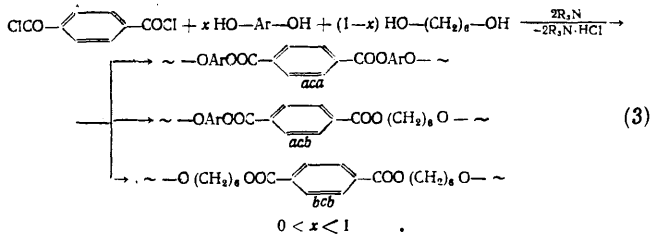
increasing dielectric constant of the medium. When acceptor-catalytic polyesterification is carried out in a metastable solution, the aggregation of macromolecules creates more favourable conditions for the formation of macromolecular compounds than in polyesterification in a thermodynamically stable solution with a similar dielectric constant[94]. Such aggregation of macromolecules apparently leads to a local increase of the concentration of the terminal groups of the polymer chains, which causes, on the one hand, an increase of the rate of propagation of macromolecules, and, on the other hand, diminishes the contribution of side reactions.

The precipitation of the polymer from solution under the conditions of acceptor-catalytic polyesterification does not in principle prevent further increase of its molecular weight, which takes place owing to the interaction of the terminal groups of the macromolecules with one another and with the initial compounds[94,96,97]. The optimum conditions for the synthesis of polyarylates in a heterogeneous system are a high solubility of the initial compounds in the reaction medium, an appreciable swellability of the polymer in a weakly polar medium, or a high polarity of the medium when the swellability of the polymer in the solvent is insignificant[97].

Acceptor-catalytic polyesterification in a heterogeneous system is of considerable practical interest, since the technological scheme of the synthesis of polymers is then significantly simplified.

IV. CHARACTERISTICS OF THE SYNTHESIS OF COPOLYMERS IN A HOMOGENEOUS SYSTEM

The successful discovery of the laws of formation of macromolecules under the conditions of non-equilibrium polycondensation depends in many respects on the extent to which the fundamental rules controlling the formation of fixed polymers have been found. The problems of the composition and structure of both polycondensation and polymerisation copolymers are especially important in this respect. Up to 1972, there were no experimental data for the influence of various factors on the composition and structure of copolymers obtained by non-equilibrium copolycondensation in a homogeneous system. In 1972 Korshak and coworkers[98,99] published for the first time experimental data concerning the rules governing the formation of the macromolecules of mixed polymers under the conditions of non-equilibrium copolycondensation in solution in relation to joint acceptor-catalytic polyesterification of a bisphenol and a glycol (comonomers) with terephthalic acid dichloride (the intermonomer).



(3)

The relative contents of the homo-(*aca*, *bcb*) and hetero-(*abc*) triads in the copolyesters were determined by high-resolution ^{1}H NMR.[98-104] The parameter K_M—the coefficient of the microheterogeneity of the copolymer—was calculated from the results[105,106]. $K_M = 0$ for a mixture of two homopolymers, $K_M = 1$ for statistical copolymers, and $K_M = 2$ for regularly alternating copolymers. Consequently the absolute values of the deviations of K_M from unity may make it possible to infer in quantitative terms the degree of order in the distribution of units, block copolymers being located in the region where $0 < K_M < 1$.

Interesting experimental data were obtained in the study of the structure of copolymers obtained when copolyesterification is carried out in solution by a single-stage method, in which the intermonomer and comonomer are in solution at the beginning of the reaction[98,101-104]. It was established that, regardless of the difference between the activities of the comonomers, copolymers are formed with a nearly statistical distribution of units (Table 3, Nos. 1 and 3). For low degrees of reaction, the composition of the copolymer is enriched in units containing the more active comonomer, but, as the copolyesterification reaction proceeds, the number of units becomes equal to the initial molar ratio of the comonomers[106]. Copolymers with a statistical distribution of units have been obtained also in two-stage copolycondensation, where the second comonomer was introduced into the reaction sphere only after the completion of the polycondensation of the intermonomer with the first comonomer, i.e. under conditions simulating an infinitely large difference between the activities of the comonomers (Table 3, Nos. 2 and 4).[100] It was shown that certain deviations from the statistical distribution of units in the macromolecules are caused by a change in the activity of the second COCl group of the intermonomer after the first COCl group has reacted (Table 1). These results demonstrated the erroneous nature of the view according to which statistical copolymers are difficult to obtain by non-equilibrium copolycondensation of comonomers with different activities[8,10,107].

Table 3. The structure of copolyterephthalates based on a bisphenol and hexamethylene glycol and obtained by joint acceptor-catalytic polyesterification in the presence of triethylamine (dichloroethane, 40°C).

No.	Bisphenol	Copolymerisation constant for comonomers q	Content of triads, mole fraction			K_M
			aca	*acb*	*bcb*	
1	2,2-di-(4-hydroxy-3-methylphenyl)propane*	5.3[103]	0.19	0.62	0.19	1.24
2	ditto**	∞	0.19	0.64	0.17	1.28
3	2,2-di-(3-chloro-4-hydroxyphenyl)-propane*	33[103]	0.22	0.56	0.22	1.12
4	ditto**	∞	0.25	0.54	0.21	1.09

*A solution of terephthalic acid dichloride (0.2 M), the bisphenol (0.1 M), and hexamethylene glycol (0.1 M) was treated with triethylamine (0.4 M) and the copolyesterification was continued for 1 h.[103]

**A solution of terephthalic acid dichloride (0.2 M) and the bisphenol (0.1 M) was treated with triethylamine (0.4 M). After 30 min, hexamethylene glycol (0.1 M) was introduced into the reaction mixture and the reaction was continued for 1 h.[100]

It was found that block copolymers can be obtained under the conditions of single- and two-stage acceptor-catalytic copolyesterification when the intermonomer is gradually introduced into the reaction zone (Table 4).[99-104]

In this case the length of the blocks increases with increasing difference between the activities of the comonomers and with decrease of the rate of entry of the intermonomer into the reaction zone. A convenient method for the synthesis of block copolymers is three-stage copolycondensation, where the acceptor-catalytic polyesterification of the intermonomer with each comonomer is carried out in different reaction volumes. The intermonomer in one reaction volume is introduced in an excess, while in the other it is present in a deficiency in relation to the monomer, the amounts being calculated so that the overall molar amounts of the functional groups of the intermonomer and the comonomers in the two reaction volumes are equal[103]; at the end of the reaction the first and second systems are combined. It was found that the smaller the deviation from equivalence in each system, the greater the length of the blocks in the block copolymers.

Table 4. The structure of copolyterephthalates based on a bisphenol and hexamethylene glycol, obtained by single-stage copolyesterification in the presence of triethylamine with gradual introduction of terephthalic acid chloride into the reaction solution (dichloroethane, 40°C).[99]

Bisphenol	q^{103}	Length of blocks		K_M
		n_{ac}	n_{bc}	
2,2-di-(4-hydroxy-3-methylphenyl)propane	5.3	4.4	4.4	0.46
9,9-di-(4-hydroxylphenyl)fluorene	12.6	5.6	5.6	0.36
2,2-di-(4-hydroxy-3-nitrophenyl)propane	31	8.2	8.5	0.24
2,2-di-(3-chloro-4-hydroxyphenyl)propane	33	9.2	9.2	0.22

By varying the above factors, it is possible to obtain block copolymers with different lengths of the blocks, regulating thereby the structure of the macromolecules of mixed polymers in the required way.

Experimental data for the influence of various factors on the composition and structure of copolymers were confirmed by the fundamental conclusions arising from the quantitative theory of non-equilibrium copolycondensation in a homogeneous system developed by Kuchanov[105, 106, 108]. A satisfactory quantitative correspondence between the experimental and theoretical data was established, the difference between them being within the limits of the experimental error (see, for example, Table 5). This shows that the conclusion reached from the results of the study of joint acceptor-catalytic polyesterification are of general validity and apply satisfactorily to the formation of the macromolecules of copolymers under the conditions of non-equilibrium copolycondensation in a homogeneous system.

Table 5. The values of K_M for copolyterephthalates synthesised by two-stage copolycondensation (dioxan, 40°C)*[83].

X in 2,2-di-(4-hydroxy-3-X-phenyl)propane	x***	K_M (expt.)	K_M (theor.)
CH_3	2.45	1.28	1.33
Cl	1.13	1.09	1.05
NO_2	0.77	0.93	0.91

* See second footnote to Table 3.
** See Table 1.

By surveying the experimental data, it was possible to formulate the fundamental characteristics of the formation of the macromolecules of mixed polymers under the conditions of non-equilibrium copolycondensation in a homogeneous system[98-104, 106].

1. When the entire amount of the intermonomer is introduced at once into the reaction zone at the beginning of non-equilibrium copolycondensation, statistical copolymers are formed regardless of the difference between the activities of the comonomers. The use of a bifunctional compound with dependent functional groups as the intermonomer influences the structure of the copolymers: the decrease of the activity of the second functional group after the first has reacted leads to an increase of the fraction of regularly alternating fragments in the polymer chains; the increase of the activity of the second functional group of the intermonomer promotes an increase in the length of the blocks.

2. The introduction of comonomers into the reaction zone in stages is not a sufficient condition for the synthesis of copolymers with a block structure.

3. The synthesis of block copolymers by single-stage non-equilibrium copolycondensation in a homogeneous system requires that the activities of the comonomers should be different and that the rate of introduction of the intermonomer into the reaction zone should be smaller than the rate of its interaction with the more reactive comonomer.

V. CHARACTERISTICS OF THE SYNTHESIS OF POLYESTERS FROM DIOLS WITH AN ASYMMETRIC DISTRIBUTION OF HYDROXY-GROUPS

The non-equilibrium polycondensation of bifunctional compounds with an asymmetric distribution of functional groups (z–RS–z) gives rise to the problem of the determination of the structure of heterounit polymer chains, and to the possibility of additions of the "head-to-head" ("tail-to-tail") or "head-to-tail" type:

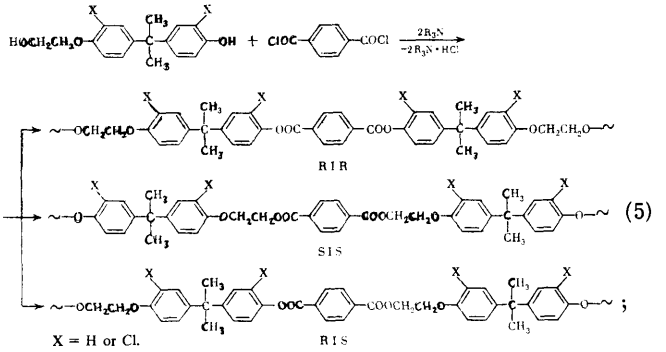
$$z\text{–RS–}z + y\text{–I–}y \rightarrow \begin{cases} \sim\text{–RS–I–RS–I–RS–I–}\sim + 2xy \\ \text{"head-to-tail"} \\ \sim\text{–RS–I–SR–I–RS–I–}\sim + 2xy \\ \text{"head-to-head", "tail-to-tail"} \end{cases} \quad (4)$$

Here z–RS–z and y–I–y are bifunctional monomers with asymmetric and symmetrical distributions of functional groups respectively. This type of problem arises in the polymerisation of asymmetric vinyl monomers, for example, monosubstituted ethylenes, in which heterounit macromolecules with "head-to-head" or "head-to-tail" distributions of units are also formed. This problem has been fairly well investigated in polymerisation and it was established that the "head-to-tail" addition occurs more frequently[109, 110].

There have been a number of studies[111-116] in which the problem of the structure of polycondensation polymers based on the monomers shown in Eqn. (4) is discussed,

and the possibility of "head-to-head" or head-to-tail" additions is considered. The view is expressed in these studies that the different activities of the functional groups in z–RS–z is the decisive factor in the formation of monomers in which "head-to-head" additions predominate.

In 1974 Korshak et al.[117] published the first study where they established the structure of polymers based on monomers with an asymmetric distribution of functional groups, in relation to the acceptor-catalytic polyesterification of the β-hydroxyethyl ethers of bisphenols with terephthalic acid dichloride, and determined the fundamental principles of the formation of their macromolecular structure[117,118]:



(5)

The structure of the polyesters was studied by high-resolution ^{1}H NMR, based on the different chemical shifts of the phenylene protons in the terephthalic acid residue in homo-(RIR, SIS) and hetero-(RIS) triads corresponding to the "head-to-head" ("tail-to-tail") or "head-to-tail" addition respectively[117,118]. The coefficient of microheterogeneity K_M served as a quantitative characteristic of the regularity of the structure of the macromolecules. For regularly alternating polymers of the "head-to-head" and "tail-to-tail" type, $K_M = 0$, while for polymers involving "head-to-tail" additions, $K_M = 2$. $K_M = 1$ corresponds to a statistical distribution of units in macromolecules.

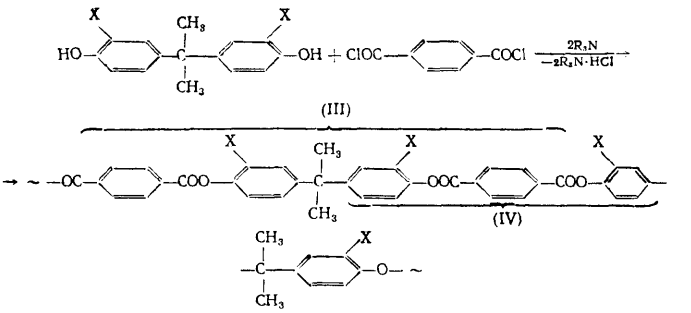
It was established that, when both initial monomers are in solution at the beginning of polycondensation, a polymer with a nearly statistical distribution of units is formed regardless of the difference between the activities of the hydroxy-groups ($K_M = 1.01–1.11$).[117,118] This result showed that, even a considerable difference between the reactivities of the phenolic and alcoholic groups, does not constitute a sufficient condition for preferential addition of the "head-to-head" type. The deviation of K_M from unity is apparently due to the fact that the activity of the second COCl group of terephthalic acid dichloride diminishes after the first COCl group has reacted[83], which leads to a predominance of the "head-to-tail" structures[117]. It has also been established that the formation of polymers with "head-to-head" ("tail-to-tail") structures, predominating under the conditions of non-equilibrium polycondensation, requires a gradual addition of a monomer with a symmetrical distribution of functional groups (terephthalic acid dichloride) to a solution of the monomer with an asymmetric distribution of functional groups (the diol). K_M depends on the rate of addition of the acid dichloride and on the difference between the activities of the OH groups of the diol[117,118].

Analysis[117], has shown that the kinetic mechanism of the above process (and hence its mathematical description) is the same as the mechanism described earlier in connection with calculations on copolycondensation[105,106,108,119]. The experimental and theoretical characteristics of the formation of the structures of the polymer chains based on monomers with a "head" and a 'tail" agree satisfactorily[117].

VI. SYNTHESIS OF CONFORMATIONALLY REGULAR POLYARYLATES

An interesting feature of acceptor-catalytic polyesterification is conformational specificity of this process, which makes it possible to obtain conformationally regular polymers whose conformational tacticity is established in the course of the reaction, and the macromolecules contain regular sequences of one or other (but fully defined) rotational isomer in the monomer residue[120,121].

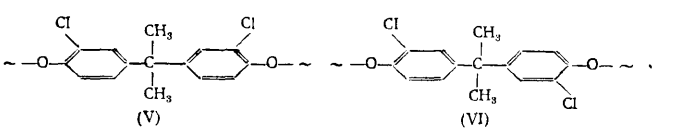
The study of the kinetics, mechanism, and characteristics of acceptor-catalytic polyesterification and of the properties of the polymers obtained enabled Korshak et al.[122] to establish for the first time in 1970 that non-equilibrium polycondensation gives rise to considerable possibilities for the synthesis of stable stereoregular polycondensation polymers of a new type, whose macromolecules contain regular sequences of stable rotational isomers. Conformationally regular polyarylates of the above type were synthesised under the conditions of acceptor-catalytic polyesterification from *o,o'*-disubstituted, 2,2-di-(*p*-hydroxyphenyl)propane and terephthalic acid dichloride[57,123–126]:



(6)

The fundamental novelty of the synthesis of conformationally-regular polymers under the conditions of acceptor-catalytic polyesterification is the fact that their regular three-dimensional microstructure is formed directly during the growth of macromolecules.

Conformational analysis by ^{35}Cl NQR of the polyterephthalates of 2,2-di-(3-chloro-4-hydroxyphenyl)propane (dichlorodian) as well as compounds (III) and (IV) (X = Cl), simulating the fragments of the polymer chain, showed that, depending on the conditions of synthesis, the macromolecules of the given polyarylate contain regular sequences of cisoid (V) or transoid (VI) rotational isomers of the bisphenol residue[57,124,125]:



It was established that the microstructure of conformationally regular polyarylates is influenced by the structure of the initial compounds (bisphenols, dicarboxylic acid dichlorides, and tertiary amines) and by the conditions of acceptor-catalytic polyesterification[121–127].

Comparison of the properties of polyterephthalates based on di-(3-chloro-4-hydroxyphenyl)alkanes with different bridge groups showed that the decrease of the barrier to rotation about the $C_{(1)}-C_{(2)}$ bonds, where $C_{(1)}$ and $C_{(2)}$ are respectively the carbon atoms of the bridge group and the benzene ring, in the sequence $C(CH_3)_2 > C(CH_3)(C_7H_{15}) > C(CH_3)_2 > CH_2$ promotes the formation of conformationally regular polyarylates, the high stereotacticity of which in the case of the methylene bridge is apparently caused not so much by the conformational specificity of acceptor-catalytic polyesterification as by the ready crystalisability of such polymers[125,127]. Thus, regardless of the conditions of synthesis, crystalline polyterephthalates of di-(3-chloro-4-hydroxyphenyl)-methane contain only one type of conformational isomer of the bisphenol residue.

The use of sterically hindered bisphenols [di-(5-chloro-2-hydroxyphenyl)alkanes] in acceptor-catalytic polyesterification made it possible to obtain conformationally regular polyarylates with a high degree of order in their structure[125,127]. It has been suggested that the considerable stereotacticity of these polymers is due to the energetic non-equivalence of different conformations in the bisphenol residue, which leads to the formation of macromolecules containing mainly one conformation of the bisphenol fragment.

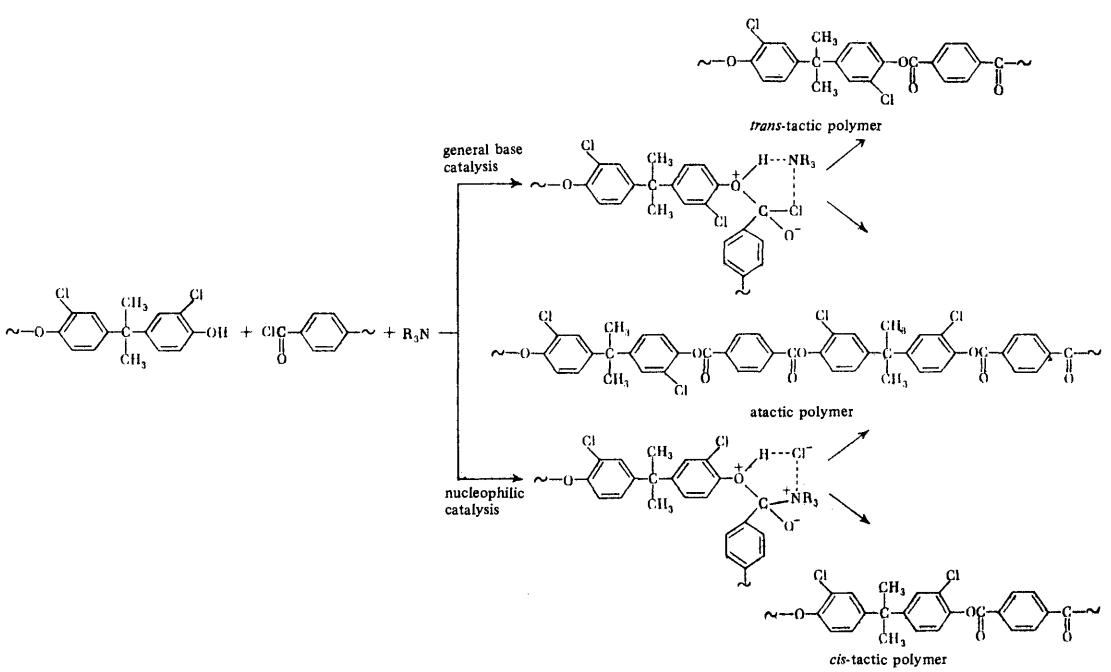
A characteristic example of the conformational specificity of acceptor-catalytic polyesterification is the synthesis of conformationally regular dichlorodian polyarylates based on various dicarboxylic acid dichlorides[126] in the presence of various tertiary amines[57,125,126]. It was established that, depending on the nature of the tertiary amine (primarily depending on its basicity) and hence depending on the reaction mechanism (nucleophilic or general base catalysis)[57,66-68], macromolecules containing one or other type of rotational isomer are formed. In the presence of weakly basic heterocyclic tertiary amines (nucleophilic catalysis) polymers with *cis*-isomers (V) of the bisphenol fragment are formed, whereas in the presence of highly basic trialkylamines (general base catalysis) the products are polymers with *trans*-isomers (VI).[125] Korshak and coworkers[57,125] attribute the cause of this phenomenon to the different geometries of the transition complexes corresponding to the nucleophilic and general base catalysis, which promotes the formation of different rotational isomers in the bisphenol residue [see Eqn. (7)].

A significant factor is that, in the crystallisation of amorphous polyarylates by a secondary treatment, polymers containing only the *trans*-isomers (VI) in the macromolecules are formed, whereas under the conditions of acceptor-catalytic polyesterification polymers with both cisoid and transoid isomeric forms of the dichlorodian residue may be produced. The role of the acceptor-catalyst in the establishment of the conformational tacticity of polyarylates apparently consists in determining the relative contributions of the two catalytic processes competing in the reaction, which leads in its turn to the predominance in the polymer chains of one or other rotational isomer.

Korshak and coworkers[121-127] showed that the presence of regular sequences of isomeric forms in polyarylate macromolecules influences significantly their properties. In particular, an increase of the stereotacticity of the polymers increases the degree of their crystallinity and the softening temperature, and diminishes their solubility.

The study of the influence of the conditions of synthesis and subsequent treatment of conformationally regular polyarylates on their properties showed a fairly high stability, including their state in solution, of the conformations of the bisphenol residue in the polymer chains[27,121,123,124,128]. Under the influence of mechanical, thermal, and other influences, there is a possibility of the conversion of conformationally regular polymers into conformationally atactic polymers[57,121,123,124].

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(7)

Thus the data presented in this review show that acceptor-catalytic polyesterification is of considerable interest as a method of synthesis of homogeneous and mixed polyesters with a definite macromolecular structure, including conformationally regular polyarylates.

Acceptor catalytic polyesterification has acquired particular importance as a model reaction for the investigation of the characteristics of the formation of the macromolecules of copolymers and polymers containing "head-to-tail" fragments under the conditions of non-equilibrium polycondensation in a homogeneous system. There are at present virtually no literature data concerning the characteristics of the formation of macromolecules of this type under the conditions of non-equilibrium polycondensation in a heterophase system. Studies on the characteristics of acceptor-catalytic polyesterification under heterophase conditions may play a definite role in the solution of this problem. The determination of the scope of the synthesis of configurationally regular polymers under the conditions of acceptor-catalytic polyesterification, or in other words, the synthesis by acceptor-catalytic polyesterification of stereoregular polymers (for example iso- or syndio-tactic polymers) from monomers consisting of a mixture of geometrical or optical isomers, is of considerable interest.

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Some Structural and Chemical Aspects of Polycondensation

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Data concerning the influence of the structure of asymmetric monomers and monomers with bulky substituents on the structure and physicochemical properties of polycondensation polymers are compiled and analysed. The influence of the chemical structure of the monomers on the course of copolycondensation and the microstructure of the resulting macromolecules is explained.
The bibliography includes 79 references.

CONTENTS

I. Introduction 28
II. The steric structure of polycondensation polymers 28
III. The composition and structure of polycondensation copolymers 30

I. INTRODUCTION

The problem of the influence of the chemical structure of monomers on the course of polycondensation processes involving the synthesis of macromolecules and the structure of the resulting polymers has long been the subject of vigorous thorough research. Nevertheless, despite the advances achieved and the considerable number of published studies, there are still phenomena and relations in this field of the chemistry of macromolecular compounds whose nature is not clear. This is quite understandable bearing in mind that the problems of the structural and chemical relations embraces a wide range of processes, phenomena, and objects.

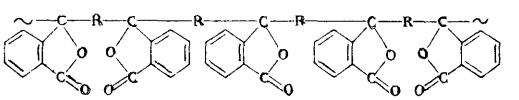
In the analysis of the structural and chemical aspects of polycondensation, it is possible to isolate two fundamental problems: (1) the influence of the chemical structure of the monomers on the reactivity of the functional groups and on the course of polycondensation; (2) the influence of the chemical structure of the monomers on the structure of the resulting macromolecules, their ability to form ordered structures, and ultimately the properties of the polymers.

Copolycondensation processes are still more complex, since, apart from the factors indicated above, the influence of the reactivity of the monomers on the microstructure of the resulting macromolecules and the influence of the microstructure of the chains of copolymers on their ability to crystallise and other properties also play a significant role.

A complete description of the structural and chemical aspects of polycondensation involves such extensive data that in the present review we shall deal only with problems of polycondensation with participation of asymmetric monomers and monomers containing bulky substituents. Polymers with interesting structures, having a set of valuable physicochemical properties, have been obtained on the basis of these monomers. Part of the review is devoted to the problem of the influence of the reactivity of the functional groups of monomers on the course of joint polycondensation processes and the microstructure of polymer chains, which makes it possible to relate the physicochemical properties of polymers to the microstructure of their macromolecules.

II. THE STERIC STRUCTURE OF POLYCONDENSATION POLYMERS

A characteristic feature of the majority of polymers obtained by polycondensation methods is the symmetrical structure of the monomers employed; the stereoregularity of the structure has therefore not been investigated for a long time. However, as in the synthesis of polymers by polymerisation methods, one can foresee the possibility of the synthesis of stereoregular polymers by polycondensation methods. The principal essential condition for this purpose is known to be the use of monomers capable of forming asymmetric units. Thus the employment of optically active monomers makes it possible to synthesise polymers with a sterically regular alternation of fragments. The use of monomers containing carbon atoms with two different and two identical substituents yields atactic polymers. The polyarylates obtained from phenolphthalein and different dicarboxylic acids are an example of polymers of this type[1-7]. The following schematic formula illustrates the structure of an atactic polyarylate of this kind:



According to Korshak and coworkers[8-16], when ring-substituted bisphenols are used, polymers having various crystallographic forms are produced under the conditions of acceptor-catalytic polyesterification, depending on the nature of the solvent and the tertiary amine. The polyarylate obtained from 2,2-di-(3-chloro-4-hydroxyphenyl)-propane and terephthalic acid in the presence of pyridine is crystalline and gives rise to narrow NQR signals. This was the first stereoregular polymer of this type obtained by polycondensation. The use of the dichlorides of isophthalic and 1,1'-oxybisbenzene-4,4'-dicarboxylic acid instead of the dichloride of terephthalic acid leads to a decreased degree of crystallinity of the polymers and a consequent improvement of their solubility. A general feature has been observed for all the acid dichlorides employed—the precipitation of the polymer from the reaction mixture (dioxan, dichloroethane, acetone, and nitrobenzene) during synthesis promotes the formation of

polyarylates with a high degree of crystallinity (stereoregularity) compared with the polymers which remain in solution. Korshak and coworkers established that a decrease of the distance between the carbonyl groups in the acid fragment has a favourable influence on the crystallisability of the polymers, which is apparently associated with the increased regularity of the macromolecular structure.

Korshak[1-4] postulates that polymers with a regular structure and without defects (anomalous fragments) in their macromolecules should have more close-packed chains, should crystallise more readily, and should possess more effective mechanical and physical properties than polymers with a non-regular structure. This is to some extent confirmed by data concerning the dependence of the melting points of the copolymers on the amount of the second monomer introduced into the copolymer. If the treatment is confined to a consideration of those copolymers which contain only small amounts of the second monomer, then the melting point is found to decrease with increasing content of the second monomer, i.e. the monomer which increases the number of anomalous fragments in the polymer chain.

Chemical defects in macromolecules are also an important factor determining the ability of polymers to crystallise. The greater the number of defects, the greater the irregularity of the macromolecules, and the smaller the capacity of the polymer for crystallisation, other conditions being equal.

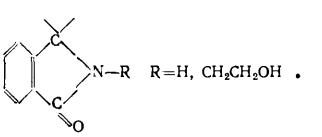
The influence of the chemical structure of the initial monomers on the ability of polycondensation polymers to crystallise is manifested in many instances. This phenomenon can be illustrated in a particularly interesting manner in relation to cardo-polyarylates. A large number of cardo-polyarylates, containing cardo-groups such as the phthalide, phthalimidine, fluorene, anthrone, cyclohexane, norbornane, and other groups, have been synthesised by polycondensation[1-37]. Cardo-polyarylates are obtained by non-equilibrium polycondensation: low-temperature (acceptor-catalytic) polycondensation[1-19,23-30], high-temperature polycondensation in solution[6,7,19,31,32], and interfacial polycondensation[1-6,17-23]. In interfacial polycondensation account must be taken of the specific behaviour of cardo-monomers of the phenolphthalein type in aqueous alkaline media. However, Morgan[18] and Korshak and coworkers[20-23] established that conversion of phthalide derivatives into phthalimidine derivatives makes it possible to synthesise macromolecular polyarylates by interfacial polycondensation. The use by the authors of phthalimidine derivatives such as phenolphthalein imide and 2-β-hydroxyethyl-3,3-di-(4-hydroxyphenyl)phthalimidine, containing functional groups with appreciably different reactivities, leads to the formation by interfacial polycondensation of cardo-polymers with free >NH and NCH_2CH_2OH groups respectively, which permits their chemical modification. The joint polycondensation of the above bisphenols and the dichloride of isophthalic or terephthalic acid results in the formation of a cross-linked copolymer under certain conditions.

Acceptor-catalytic polycondensation has come to be widely used in recent years as a method for the synthesis of cardo-polyarylates[1-19,24-30]. Korshak and coworkers[10,11,25,30] obtained by this method phenolphthalein polyterephthalates. The synthesis was carried out in a medium (dichloroethane) in which the polymer is soluble and in a medium (acetone) from which the polymer is precipitated during synthesis. It was established that the nature of the solvent employed affects the molecular weight of the polymer, as low-temperature polyesterification in a metastable solution (a mixture of the solvent and precipitant) leads to the formation of polyarylates with a narrow molecular-weight distribution[12]. The yield and molecular weight of the polyarylate depend appreciably on the sequence in which the monomers are introduced[14,26].

Many cardo-polyarylates have been synthesised by the high-temperature polycondensation of dicarboxylic acid dichlorides and bisphenols in organic solvents. The study of the kinetics of the reaction of terephthalic acid dichloride with 9,9-di-(4-hydroxyphenyl)fluorene and certain bisphenols of the type of norbornane enabled Korshak and coworkers[31,32] to suggest an ionisation mechanism for this reaction. It was established that the polycondensation of phenolphthalein and dicarboxylic acid dichlorides in ditolylmethane leads to the formation of polymers which are precipitated from solution. The synthesis of such polyarylates in more polar chlorinated solvents or nitrobenzene takes place in solution, according to Korshak and coworkers[6,7], with formation of polymers having better physicomechanical properties. This phenomenon was explained by the fact that, in a medium dissolving the polymer, macromolecules having uncoiled rigid conformations and giving rise to a fibrillar structure are formed, whereas the polymer obtained in ditolylmethane gives rise to irregular globular structures. Thus in the synthesis of polymers with rigid macromolecular chains it is necessary to take into account the influence of the reaction medium on the formation of the corresponding conformations.

All the cardo-phenolphthalein polyarylates are amorphous non-crystallising polymers. Korshak and coworkers[2-5] suggest that their structure is analogous to that of atactic polymers. However, one must assume that under certain conditions it is possible to obtain a crystalline stereoregular phenolphthalein polyarylate. The possibility is indicated by the finding that the cardo-polyarylates formed by di-(4-hydroxyphenyl)fluorene and 9,9-di-(4-hydroxyphenyl)-10-anthrone with terephthalic acid crystallise and the conditions of their synthesis influence, according to Vinogradova et al.[33], not only the molecular weight of the polyarylates but also their structure.

Studies by Korshak and coworkers[22,23] showed that, by using an appropriate solvent, it is possible to synthesise a stereoregular crystalline cardo-polyarylate containing asymmetric groups. Thus, crystalline phthalimidine polyarylates containing NH groups have been synthesised. The formation of the crystalline structure of the polymer is probably associated with decreased solubility of the given polyarylate and increased rigidity of its macromolecules by hydrogen bonding between the phthalimidine groups and the electron-accepting groups of the macromolecules. This effect is manifested even more clearly in *N*-β-hydroxyethylphthalimidine:



During recent years much attention has been devoted to cardo-polyarylates containing carborane rings[34-37]. The carborane-containing polyarylates obtained by Korshak and coworkers are characterised by an increased thermal stability, a high degree of order in their structure, and other properties of practical interest.

Investigations have established that a mixed crystalline polyarylate may be obtained when even one of the monomers is capable of forming a crystalline homopolyarylate and this monomer is taken in a large excess [38].

The data presented show that the chemical structure of the monomers and particularly the presence of asymmetric bulky substituents influence significantly not only the course of the process but also the structure and properties of the polymers obtained.

III. THE COMPOSITION AND STRUCTURE OF POLYCONDENSATION COPOLYMERS

1. General Postulates

A significant change in the properties of polymeric materials obtained by polycondensation can be achieved by synthesising copolymers, i.e. by carrying out the joint polycondensation of a large number of monomers.

The physicochemical characteristics of copolymers are in many respects determined by their chemical composition by the inhomogeneity of their composition, and by the different chemical structures of the macromolecular chains. Without considering here the important factor of the average chemical composition, on which the properties of the copolymer depend significantly, one should note that the chemical inhomogeneity and the inhomogeneity of the structures of macromolecules are very important, although it is very difficult to control them in the course of the synthesis.

The inhomogeneity of chemical composition is associated with the presence in the copolymer macromolecules of different elementary units in different proportions. In polycondensation copolymers, which are the subject of the present review, an inhomogeneity of the composition is observed, but it is not as important as for polymerisation copolymers. The stepwise nature of the copolycondensation process and the occurrence of reactions between macromolecules promote an equalisation of the compositions of the individual macromolecules formed in the early stages of the process. Nevertheless the results of fractionation studies have shown that the chemical composition of polycondensation copolymers is inhomogeneous [39,40].

Another problem concerning the microstructure (microheterogeneity) of copolymer chains is associated with the different ways in which the corresponding units alternate along the macromolecular chain. Even copolymers with identical molecular weights and identical chemical compositions may differ appreciably in the distribution of units and their sequence. A quantitative estimate of the microheterogeneity of copolymers involves the measurement of the relative contents of the corresponding chain units having a definite chemical structure. Modern research methods make it possible to determine the sequence of only small fragments of the chain—with a length not exceeding 3–4 units. Analysis of the sequence of units throughout the macromolecule is based on the hypothesis that the processes responsible for the chain microstructure are entirely random. The experimental determination of the alternation (sequence) of units in copolymer chains is based on the measurement of a property of the polymer which depends on the number of units of definite types and on the order in which they are joined together. Depending on the nature of the copolymer investigated, such a property may be, for example, the absorption intensity at certain frequencies in the ultraviolet or infrared regions, the melting point, the glass point, and the presence of chemical functional groups characteristic of a given structure [41,42]. High-resolution NMR has acquired the greatest importance in recent years in the study of the microstructures of copolymers. The relative intensities of the signals of the corresponding nuclei make it possible in many instances to determine accurately the fraction of chemical groups characteristic of a particular type of alternation.

The properties of the copolymer depend strongly on the sequence of units in its macromolecules; this applies particularly to the extreme cases of the distribution of elementary units. If it is assumed that the copolymer is made up to two types of main units c_1 and c_2, their distribution may be as follows:

(a) a distribution characterised by the maximum number of linkages between the units c_1 and c_2. This sequence corresponds to a regularly alternating structure of the copolymer chain:

$$\sim -c_1-c_2-c_1-c_2-c_1-c_2-\sim;$$

(b) a distribution distinguished by the maximum number of linkages between units of one type. Such a sequence corresponds to a block structure of the copolymer chain:

$$\sim -c_1-c_1-c_1-c_1-c_2-c_2-c_2-c_2-\sim;$$

(c) chains with an intermediate distribution of units may manifest a tendency towards irregular alternation or to a block structure, or their structure may be completely disordered:

$$\sim c_1-c_1-c_2-c_1-c_2-c_2-c_2-c_1-c_1-c_2-\sim .$$

A copolymer with a completely disordered distribution of units is called a statistical copolymer.

The problem of the sequence of units in polycondensation copolymers has been the subject to theoretical considerations long before the development of experimental methods permitting the study of the microstructure of copolymers. A mathematical treatment of the problem was published as early as the 1950s by Case [43] and Beste [44]. In subsequent years the studies by Yamadera and Murano [45] and Kuchanov and coworkers [46,47] assumed a considerable importance.

A quantitative description of the microheterogeneity of polycondensation copolymers may be achieved in two ways. Like polymolecularity or the inhomogeneity of composition, microheterogeneity is described with the aid of the corresponding distribution function. The distribution functions for both types of units make it possible to describe exactly the nature and degree of order in the chemical structure of chains. A theoretical treatment of this problem has been described by Beste [44] and Kuchanov [48].

Another widely used method for the description of the microheterogeneity of copolycondensation products is based on a numerical characteristic of the degree of order in the structure of copolymer chains. The method of numerical estimation of the chemical structures of polycondensation copolymers from high-resolution NMR data, used by the majority of workers, was first introduced in the classical study of Yamadera and Murano [45]. They investigated the microheterogeneity of copolyesters obtained by the high-temperature copolycondensation of glycols with dimethyl dicarboxylates and also the nature of the changes in microheterogeneity owing to exchange reactions between poly(ethylene terephthalate) and poly(ethylene sebacate). Yamadera and Murano [45] developed a method for the estimation of the degree of

order in the chemical structure of copolymer chains in relation to the copolyester obtained by the latter reaction. For example, the chains of the copolymer obtained from ethylene glycol (G), dimethyl terephthalate (T), and dimethyl sebacate (S) may contain three types of diads — two homodiads T–G–T and S–G–S and one heterodiad T–G–S. The intermonomer G, which joins together the T and S comonomers in the chains, has different environments in the above diads, which induces the appearance of three different signals in the NMR spectra. The intensity of these signals enabled the authors to determine the mole fractions of the terephthalate x_T and the sebacate x_S:

$$x_T = \frac{S_{TGS}}{2} + S_{TGT}, \quad (1)$$

$$x_S = \frac{S_{TGS}}{2} + S_{SGS}, \quad (2)$$

where S_{TGT}, S_{SGS}, and S_{TGS} are the fractions of the above diads respectively.

The probability of the appearance in the copolymer chain of the T unit after the S unit is defined by the relation

$$P_{TS} = \frac{S_{TGS}}{2x_S}; \quad (3)$$

and the probability of the appearance of the S unit after the T unit is correspondingly

$$P_{TS} = \frac{S_{TGS}}{2x_T}. \quad (4)$$

According to Yamadera and Murano[45], the quantity characterising the microheterogeneity of the copolymer is the sum of the above probabilities. These workers denoted the above quantity by B and called it the degree of randomness. Kuchanov[46] called the same quantity the coefficient of microheterogeneity (K_M) and Slonim and coworkers[49] used the term "coefficient of non-regularity". For the example under discussion,

$$K_M = B = P_{ST} + P_{TS} = \frac{S_{TGS}}{S_{TGS} + 2S_{TGT}} + \frac{S_{TGS}}{S_{TGS} + 2S_{SGS}}. \quad (5)$$

When $K_M = 1$, the arrangement of the T and S units in the chains is disordered. If $K_M < 1$, there is tendency towards the formation of blocks. The quantity $K_M = 0$ corresponds to a mixture of homopolymers. When $K_M > 1$, the number of consecutively connected diads of the same type diminishes and the limiting case $K_M = 2$ corresponds to a regularly alternating copolymer. The number-average lengths of the sequences of T and S units are respectively

$$\bar{L}_{nT} = \frac{2x_T}{S_{TGS}} = \frac{1}{P_{TS}}. \quad (6)$$

$$\bar{L}_{nS} = \frac{2x_S}{S_{TGS}} = \frac{1}{P_{ST}}. \quad (7)$$

Consequently

$$K_M = \frac{1}{\bar{L}_{nT}} + \frac{1}{\bar{L}_{nS}}. \quad (8)$$

However, these equations are valid only when any macromolecule contains a fairly large number of units.

Experimental conclusions reached from the study of Yamadera and Murano[45] under consideration concern the microheterogeneity of the copolymers obtained by copolycondensation and exchange reactions. Since the values of K_M calculated from NMR data for the above copolymers are close to unity, the authors speak of a random distribution of units in the macromolecules obeying the Bernoulli statistics.

When the method proposed by Yamadera and Murano[45] is used, one must not forget that the coefficient of microheterogeneity K_M can serve only as a very approximate characteristic of the alternation of units in the copolymer chains and that its value does not in many instances yield an exact idea about the real macromolecular structure. An example illustrating the ambiguity of the description of the chain structure with the aid of the K_M coefficient has been given by Turska and Matlangiewicz[50]. According to the postulates of Yamadera and Murano, K_M close to unity indicates a random distribution of units in the copolymer chain. However, a value of K_M close to unity characterises, for example, a copolymer made up of units of two types, linked into dimeric sequences, i.e. the copolymer

$$\sim\!-c_1c_1c_2c_2c_1c_1c_2c_2c_1c_1c_2c_2-\!\sim$$

whose chain structure is entirely ordered. One can quote many similar examples. The use of a method which would permit the estimation of the distribution of units in longer chain fragments would make it possible to obtain more accurate data about the real structure of macromolecules.

Despite the ambiguity indicated above, the method of Yamadera and Murano is widely used by many workers investigating the microstructure of copolymers.

As already noted, Eqn. (8) is valid only for fairly long macromolecular chains. Since polycondensation products contain not unduly long chains, there is a risk that such simplification of the description can lead to appreciable inaccuracies. This problem has been considered by Slonim and coworkers[49], who proposed a modified method for the estimation of the microheterogeneity of chains of finite length. These workers consider a copolymer formed in the reaction between an intermonomer and two comonomers c_1 and c_2 which do not react with one another. The copolymer macromolecule can be represented schematically as follows:

$$R-(c_i)_p-(a-c_i)_n-a_q-R',$$

where R and R′ are the end groups, $i = 1$ or 2, p and $q = 0$ or 1 depending on the molar ratio of the monomers and the intermonomer, and n is the degree of polymerisation. Taking into account the above assumptions, the authors[49] derived a relation defining the coefficients K_M for the copolymer macromolecule:

$$K_M = \frac{1}{N-1}\left(\frac{N-\bar{L}_1}{\bar{L}_1} + \frac{N-\bar{L}_2}{\bar{L}_2}\right), \quad (9)$$

where $\bar{L}_1$ and $\bar{L}_2$ denote the average lengths of the block ac_1 and ac_2. For very long chains ($N \gg \bar{L}_n$), Eqn. (9) is converted into Eqn. (8).

The authors[49] used Eqn. (9) to estimate the microheterogeneity of the chains of the copolymer obtained from ethylene glycol (the intermonomer) and dicarboxylic acids — malonic and sebacic (the comonomers). According to the authors, a tendency is observed in the product towards the formation of block structures, as shown by the values of K_M, which lie in the range 0.78–0.89 for a series of experiments. It is of interest that both the

physicochemical parameters of the copolymers investigated required for the calculation of K_M (the composition and degree of polymerisation) have been determined by NMR.

Another method of characterising the microstructure of polycondensation of copolymers has been described in a theoretical study by Gritsenko[51]. The author analyses the nature of the distribution of units in copolymer chains for the simultaneous and consecutive introduction of the reactants into the reaction zone.

An important aspect of the problem of the microstructure of copolymer chains has been examined by Sawada[52,53], who defines the conditions which must be fulfilled in order that the synthesis of a polycondensation copolymer should lead to a product with a definite type of structure of macromolecular chains. Sawada characterises the degree of order in the structure of the copolymer with the aid of a parameter γ, which he introduced: $\gamma = -1$ corresponds to a block structure, $\gamma = 1$ corresponds to a regularly alternating structure, and $\gamma = 0$ corresponds to a copolymer with a statistical distribution of units in the macromolecular chains. Sawada's theory explains the statistical structure of the chains of copolymers obtained in the melt by the influence of the high process temperature. According to the author, under the conditions of low-temperature processes, there is a possibility of the formation of macromolecules with a more ordered structure.

However, the thermodynamic approach to the solution of the problem of the structure of copolymers developed by Sawada gives rise to certain objections. The author does not take into account in his treatment the dependence of the enthalpy ΔH on temperature. One can also assume that an experimental test of Sawada's theory will encounter major difficulties due to the complexity of the selection of the corresponding systems and the similarity of the temperature of low- and high-temperature copolycondensations.

The most extensive studies on the synthesis and chemical structure of polycondensation copolymers have been made in the course of many years by members of the Institute of Organoelemental Compounds of the USSR Academy of Sciences under the direction of Academician V.V. Korshak. He has made a major contribution both to the theory and practice of copolycondensation processes. Many conclusions which follow from the work of Korshak and coworkers concerning acceptor-catalytic copolycondensation can be extended also to other copolycondensation methods. Many of these studies embrace the problems of the synthesis of new polycondensation copolymers from various monomers. Another field of study is associated with the determination of the chemical structure of copolycondensation products. The influence of various factors, particularly factors such as the reactivity of the functional groups, the mode of introduction of the monomers into the reaction medium, etc., on the nature of distribution of units in the copolymers obtained by acceptor-catalytic copolycondensation has been investigated[54-56]. Together with theoretical studies, experimental investigations are being carried out at the Institute of Organoelemental Compounds on the microstructure of polycondensation copolymers by NMR.[54,57,58] The results of the theoretical and experimental research by Korshak and coworkers have been surveyed in recent years in a number of reviews[47,59,60].

In Poland studies on the synthesis and properties of polycondensation copolymers have been made by Jedlinski and coworkers[30,61,62]. The aromatic copolyesters containing bisnaphthol rings, which they obtained, are characterised, in particular, by a high thermal stability and are effective electrical insulators.

2. Kinetic Description of the Copolycondensation Process

In order to characterise the processes involving the synthesis of polycondensation copolymers, account must be taken of the fact that the copolycondensation process in all its varieties is a result of a superposition of two or more simultaneous or consecutive reactions between the functional groups. Consequently the difference between polycondensation and copolycondensation is entirely quantitative and the methods used to carry out the two processes are in principle identical. We shall therefore not consider the elements of theory and practice common to all polycondensation processes. Only certain characteristics of the kinetics of copolycondensation, associated with the simultaneous occurrence of reactions between functional groups having different reactivities, require separate consideration.

A homopolycondensation reaction can be described, after introducing certain simplifying assumptions, with the aid of simple formal kinetic equations. Taking into account these assumptions, the copolycondensation process can be regarded as a series of parallel (synchronous reactions) with participation of two or more functional groups and it can also be described by formal kinetic equations assuming that the rate of the process as a whole is determined by the rates of these reactions.

A simple example of copolycondensation is the reaction between the functional groups of three bifunctional monomers. The independent functional groups of one of the monomers are capable of reacting with the independent functional groups of the other two monomers, which are incapable of reacting under these conditions with one another. The first monomer is called the intermonomer; it binds identical or different copolymers into diads in the chains of the resulting copolymer. Having denoted the intermonomer by A and the comonomers by B and C, the structure of such a copolymer can be represented schematically as follows:

$$\cdots\text{—A—B—A—B—A—C—A—B—A—C—A—C—}\cdots$$

The copolymer is formed as a result of consecutive reactions of functional groups of type A with groups B and C, the reactions being governed by kinetic constants k_{AB} and k_{AC} respectively. If the irreversibility and second order of both reactions are assumed, the standard kinetic equations for the concentrations of the functional groups can yield relations between the compositions of the copolymer and the monomer mixture on the one hand, and the kinetic constants for the process and the initial concentrations of the monomers for different degrees of reaction, on the other[63,64]. In particular, the equation for the composition of a polycondensation copolymer becomes

$$\frac{dc_B}{dc_C} = \alpha\frac{c_B}{c_C}, \quad \alpha = \frac{k_{AB}}{k_{AC}}, \tag{10}$$

where c_B and c_C are the concentrations of the functional groups of the comonomers B and C.

The limitations of Eqn. (10) refer mainly to the limits of its applicability. Sokolov and Kurglova[65] believe that the composition equation is inapplicable to copolycondensation under homogeneous conditions in solution or in the melt. In order to attain fairly high molecular weights

of the copolymer under such conditions, not only an equimolar ratio of the reacting functional groups but also a high degree of reaction are necessary. However, when the degree of reaction is high, the composition of the copolymer becomes the same as that of the initial mixture of monomers regardless of the difference between the reactivities of their functional groups. The excess of functional groups of one type precludes, in its turn, a high molecular weight of the copolymer. According to the authors [65], Eqn. (10) can be used for copolycondensation processes at the boundary of two immiscible liquid phases, although it is known that classical kinetic equations cannot be used to describe processes occurring in heterogeneous systems.

Another limitation is associated with the identification of the monomer concentration in Eqn. (10) with the concentration of its functional groups. Evidently the concentrations of the functional groups do not change solely as a result of reactions between the monomer molecules. One should add that the equation has been obtained without taking into account the reversibility of the polycondensation reactions. The introduction of the rate constants for the reverse reactions into the kinetic equations would create significant difficulties in the calculations.

The copolycondensation process is known to be accompanied by side reactions, which can have a very significant influence on its course. The side reactions affect also the composition of the copolymer formed. In certain cases this influence may be determined exactly by an appropriate modification of the composition equation. An example of reactions in which the monomers B and C react with a compound D present in the system, apart from their reaction with the intermonomer A, is given in Sokolov's monograph [66].

One of the assumptions in the derivation of the composition equation is that the reactivities of all the functional groups are the same and do not change during the copolycondensation. However, systems in which the reactivity of a functional group depends on whether it is the first (monomer) or second (oligomer or polymer) to react are encountered much more frequently. Allowance for the different reactivities of the first and second functional groups requires, even in the simplest case, the use of a computer for the calculations.

Such calculations have been made by Sokolov and coworkers [67] for the copolycondensation of an intermonomer A with two comonomers B and C. In this process two reactions take place between the comonomers and the intermonomer and two reactions between the oligomers or polymers. The monomers and oligomers or polymers participate in the four reactions. Six kinetic equations for a process of this kind characterise the decrease in the concentrations of the individual functional groups during the reaction. The results show that the composition of the copolymer formed depends on the ratio of the reactivities of the functional groups of the monomers B and C and on the ratio of the reactivities of the first and second groups in each comonomer. The composition of the copolycondensation products is influenced significantly also by the degree of reaction. The difference between the reactivities of the first and second functional groups of the intermonomer does not affect the composition of the copolymer.

Kuchanov [46], who examined only low-temperature copolycondensation, reached similar conclusions. He believes that the rapid interchain reactions in high-temperature copolycondensation lead to a random, statistical distribution of units in the copolymer chains.

The term "copolycondensation" embraces all the processes involving the synthesis of polycondensation copolymers in which the reaction mechanism corresponds to one of the known polycondensation mechanisms and the chains of the macromolecules formed made up of two or more types of units. Even if one omits processes involving synthesis using trifunctional monomers (because they differ significantly) and the treatment is confined to the copolycondensation of bifunctional monomers, the range of the possible different versions is very wide.

The kinetic equations used to describe copolycondensation processes must contain formal expressions corresponding to a particular type of process. This requirement is valid even when different types of processes can be described by the same general kinetic relations.

The simplest copolycondensation which is most often encountered in laboratory practice is the copolycondensation of three monomers: the intermonomer A and the comonomers B and C. A correct kinetic analysis of even this not unduly complex system requires that one takes into account the mechanism of the reaction and the way it is carried out. The high-temperature copolycondensation of the above three monomers under homogeneous conditions is a kinetically simple case. However, even in this simple instance the use of formal kinetic equations requires many assumptions, the most important of which are as follows: 1) Flory's postulate that the reactivities of the terminal groups are the same and independent of the size of the macromolecule; 2) the postulate that the reacting system is homogeneous; 3) the postulate that the volume and mass of the system remain constant during the process; 4) the postulate that the reaction is irreversible under the given conditions; 5) the postulate that side reactions, primarily chain transfer reactions, do not occur under the conditions considered.

A critical consideration of each of the above postulates permits the following conclusions.

1. The hypothesis that the reactivities of the functional groups are the same is used very frequently and in principle yields a satisfactory approximation to real systems. However, it is valid also if there are no significant differences between the reactivities of the functional groups of the monomer molecules and the molecules of oligomers and polymers. The appearance of such a difference is largely caused by the structure of the monomer molecules. For example, it is known that the first OH group in ethylene glycol is more reactive than the second. After the substitution of the first group, the reactivity of ethylene glycol falls appreciably, which gives rise to significant differences in the employment of this monomer. On the other hand, bisphenols, for example, bisphenol A (dian) do not exhibit an appreciable difference between the reactivities of the first and second functional groups. The above hypothesis cannot therefore lead in all cases to a satisfactory approximation by the kinetic description to the real situation.

2. The postulate that the system is homogeneous is extremely indefinite, although it is used by all investigators of the kinetics of polycondensation in solution. In general this hypothesis is fulfilled only for a solution which constitutes a homogeneous system and must not contain a deposit (an insoluble monomer or the precipitated polymer). The evolution of a gaseous side product is as a rule neglected. However, bearing in mind that this not unduly accurate hypothesis is generally accepted for the description of homopolycondensation processes in solution

and yields a satisfactory agreement between theory and experiment, one can also adopt it for copolycondensation processes.

3. The postulate that the volume and mass remain constant throughout the process when a gaseous product is removed from the reaction system is likewise inaccurate. Despite this, many investigators employ this assumption, since the error caused by its inaccuracy is frequently small and may be disregarded. This hypothesis leads, however, to appreciable errors when a side product with a high molecular weight is removed from the process in the melt. For example, in the synthesis of the polyester from terephthalic acid dichloride and dian the relative error associated with the removal of hydrogen chloride is about 8% for the reaction in the melt. For the reaction in solution, the error diminishes by more than an order of magnitude. It can then be legitimately disregarded and one can assume with an adequate degree of approximation that the volume of the reaction mixture is constant for polycondensation in solution.

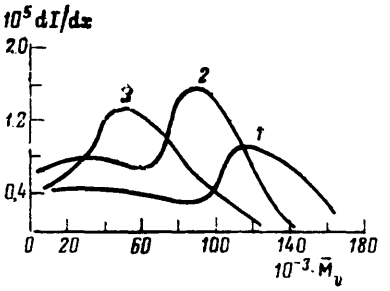


Figure 1. Differential MWD curves for a polycarbonate containing dian and inorganic compounds as admixtures: 1) specimen before heat treatment; 2) specimen heat-treated for 4 h at 260°C; 3) specimen heat-treated for 9 h at 260°C.

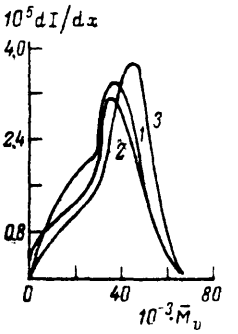


Figure 2. Differential MWD curves for a polycarbonate without admixtures: 1) specimen before heat treatment; 2) specimen heat-treated for 4 h at 260°C; 3) specimen heat-treated for 9 h at 260°C.

4. The postulate that the formation of the copolymer is a reversible reaction is in principle inapplicable to a process carried out under conditions where the equilibrium is not displaced by the constant removal of the side product from the reaction medium. However, if the equilibrium is effectively shifted towards the formation of the polymer, the above hypothesis can be adopted. One must take into account the fact that the efficiency of the displacement of the equilibrium in general diminishes with increasing degree of reaction. The hypothesis that the reaction is irreversible therefore yields an accurate description of the process for low degrees of the latter and is much less accurate for high degrees of reaction.

5. The hypothesis that there are no side reactions can also lead to major errors depending on the process conditions. Side reactions as a rule accompany polycondensation processes. However, according to literature data[60], one can select conditions such that side reactions virtually do not take place and may be disregarded. Nevertheless, this hypothesis cannot be adopted without an experimental test under the selected conditions. Presumably, under the conditions of high-temperature polycondensation in solution, the contribution of side reactions involving interchain exchange is small. Kinetics studies on the high-temperature polycondensation of dian chloroformate with dian in solution[68] showed that, under certain process conditions, chain transfer reactions may be disregarded, because their rate is too small to be measured under such conditions. These observations were confirmed subsequently in other systems. Studies on the dependence of the molecular weight distribution (MWD) of polycarbonates on the duration of their heat treatment showed in their turn that admixtures greatly influence the course of the process and the extent of side reactions[69]. In particular, it has been observed that chain transfer reactions occur in the presence of a very low content of impurities in the reaction mixture. In the absence of impurities, chain transfer reactions hardly take place. Figs. 1 and 2 show how the molecular weight distribution functions for polycarbonates, both contaminated and without impurities, vary after heat treatment. Evidently heat treatment influences appreciably only the MWD of the polycarbonate with impurities.

The above considerations suggest that, although the assumptions can lead in many cases to discrepancies between theoretical and experimental data, nevertheless there exist systems and polycondensation conditions for which they can be used without much error. Polycondensation and copolycondensation in solution under appropriate conditions may be classified as processes of this kind. This fact makes it possible to employ the fundamental equations of formal kinetics for the kinetic analysis of such processes.

We shall now consider the homogeneous high-temperature copolycondensation in solution of the intermonomer A with the comonomers B and C. Suppose that the composition of the initial monomeric mixture corresponds to equimolar proportions of the functional groups and that all the simplifying assumptions formulated above for the derivation of Eqn. (10) are valid. Using the normal kinetic equations, it is possible to derive expressions describing the time dependence of the concentrations of the individual types of functional groups[69]:

$$-\frac{dc_B}{dt}=\frac{k_{AB}c_C^0}{(c_B^0)^{1/\alpha}}c_B^{1/\alpha+1}+k_{AB}c_B^2, \qquad (11)$$

$$-\frac{dc_C}{dt} = \frac{k_{AC}c_B^0}{(c_C^0)^\alpha} c_C^{\alpha+1} + k_{AC}c_C^2, \quad (12)$$

where c_B^0 and c_C^0 are the initial concentrations of the functional groups B and C respectively. These equations can be numerically integrated on a computer for arbitrary values of the parameters. Knowing the values of c_B and c_C, it is easy to determine the degree of reaction p and the mole fractions of the bonds formed in the copolymer between the monomers A and B (x_{A-B}) and A and C (x_{A-C}):

$$p = \frac{c_B^0 + c_C^0 - c_B - c_C}{c_B^0 + c_C^0}, \quad x_{A-B} = 1 - x_{A-C} = \frac{c_B^0 - c_B}{c_B^0 + c_C^0 - c_B - c_C}, \quad (13)$$

and to obtain an equation for the kinetic curve for the process:

$$\frac{dp}{dt} = (1-p)(k_{AB}c_B + k_{AC}c_C). \quad (14)$$

3. Experimental Study of High-Temperature Polycondensation

Eqns. (11) and (12) show that the complex relation between the concentrations of the functional groups and the reaction time is evidence for the complexity of the copolycondensation processes. The concentrations of the functional groups c_B and c_C are influenced during copolycondensation by the relative reactivities of both groups in their reactions with the groups of the intermonomer and also by the initial composition of the reaction mixture. The determination of c_B and c_C as well as k_{AB} and k_{AC} (Table 1) by kinetic investigation of the corresponding polycondensation processes permits the calculation by Eqn. (14) of the theoretical $dp/dt = f(p)$ curve. Comparison of the theoretical curve and the experimental curves for the monomer A–terephthalic acid dichloride, monomer B–dian, and monomer C–tetrachlorodian [70] systems established that Eqn. (14) constitutes a satisfactory approximation for the description of the kinetics of the copolycondensation process (Fig. 3).

Table 1. The rate constants k and activation energies E for the polycondensation of terephthaloyl chloride with bisphenols in solution in α-chloronaphthalene.

Biphenol	10^3k, litre mole^{-1} s^{-1}				E, kcal mole^{-1}
	180° C	190° C	200° C	220° C	
Dian	1.19	1.78	2.78	4.40	15.3
Dimethyldian	0.49	0.85	1.29	4.10	23.6
Tetramethyldian	0.14	0.17	0.35	1.09	19.2
Tetrachlorodian	0.10	0.15	0.34	0.86	23.9
Dinitrodian	0.08	0.15	0.25	0.68	23.7

The applicability of Eqn. (14) to other systems has been demonstrated in a study of the kinetics of the copolycondensation of terephthalic acid dichloride (A) with dian (B) and phenolphthalein (C) in solution [71]. The polycondensation rate constants k_{AB} and k_{AC} were determined at 220°C in α-chloronaphthalene as 52.4×10^{-4} and 27.0×10^{-4} litre mole^{-1} s^{-1} and graphical relations between the degree of reaction and reaction time were constructed. As an example, Fig. 4 presents one of such graphs. Evidently the experimental points fit satisfactorily on the theoretical curve. Analogous relations, plotted for the copolycondensation of terephthalic acid dichloride with dian and tetrachlorodian also revealed a satisfactory agreement between the experimental and theoretical data.

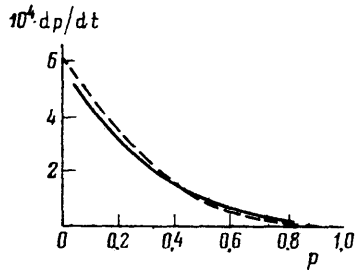


Figure 3. Dependence of dp/dt on the degree (p) of copolycondensation; continuous line—experimental curve; dashed line—theoretical curve.

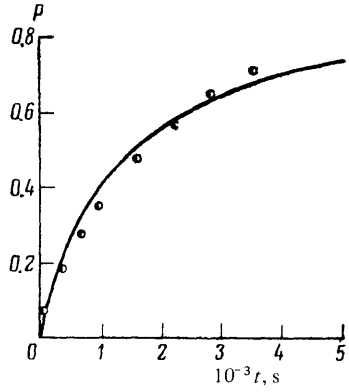


Figure 4. Dependence of the degree of reaction in α-chloronaphthalene at 220°C on the duration (t) of the copolycondensation of terephthalic acid dichloride (c_A^0 = 0.2 M) with dian (c_B^0 = 0.08 M) and phenolphthalein (c_C^0 = 0.12 M). Continuous line—theoretical curve; circles—experimental data.

The undoubted applicability of Eqn. (4) to the description of the degrees of certain high-temperature copolycondensation reactions in solution permitted its extension to an arbitrary number of comonomers (B, C, D,..., N) [73]:

$$\frac{dp}{dt} = (1-p)(k_{AB}c_B + k_{AC}c_C + k_{AD}c_D + \cdots + k_{AN}c_N). \quad (15)$$

The concentrations of the functional groups of the reacting comonomers are linked by the relation

$$\frac{c_B^0}{c_B} = \left(\frac{c_C^0}{c_C}\right)^{k_{AB}/k_{AC}}, \quad \frac{c_C^0}{c_C} = \left(\frac{c_D^0}{c_D}\right)^{k_{AC}/k_{AD}}, \ldots \quad (16)$$

Eqns. (15) and (16) were solved numerically for the copolycondensation of terephthalic acid dichloride (A) with dian (B), tetrachlorodian (C), and phenolphthalein (D) in α-chloronaphthalene at 220°C. Fig. 5 presents the dependence of the degree of copolycondensation and the concentration of the functional groups B, C, and D which failed to react on the reaction time. The most active groups are exhausted at the beginning of the processes and those with a lower reactivity at later stages. The variation of the fractions of functional groups which have not reacted with copolycondensation time can be conveniently represented graphically for the given system of monomers in an equilateral triangle. The vertices of the triangle correspond to 100% contents of the functional groups. As the copolycondensation proceeds, the fraction of less reactive groups in the reaction mixture increases (Fig. 6).

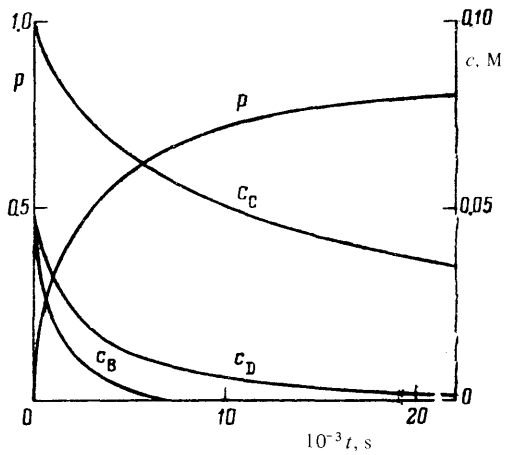


Figure 5. Dependence of the concentrations of the functional groups which have failed to react and the degree of reaction on the duration of the copolycondensation of terephthalic acid dichloride (A) with dian (B), tetrachlorodian (C), and phenolphthalein (D) at 220°C in α-naphthalene [calculated from Eqn. (16)].

It is seen from the above considerations that the nature of the variation of the chemical composition of the copolymer formed may be foreseen and its composition calculated with the aid of Eqn. (16). The composition of the copolymer obtained from terephthalic acid dichloride, dian, and tetrachlorodian has been determined experimentally and it has been established that, under the conditions of high-temperature copolycondensation in solution in α-chloronaphthalene at 220°C, the ratio of the monomers in the reaction mixture varies with reaction time [74]. Thus the study of samples of the reaction mixture by thin-layer chromatography showed that the more reactive dian virtually disappears after only 20 min of copolycondensation, while the less reactive tetrachlorodian can still be detected 80 min after the start of the reaction.

The compositions of the copolymers obtained from terephthalic acid dichloride, phenolphthalein, and dichlorodian were determined by elemental analysis.

Fig. 7 illustrates the dependence of the content of dichlorodian in the copolymers on the duration of copolycondensation. It is readily seen that, in conformity with theoretical considerations, the composition of the copolymer varies as the reaction proceeds. This phenomenon is undoubtedly associated with the different reactivities of the functional groups of the comonomers.

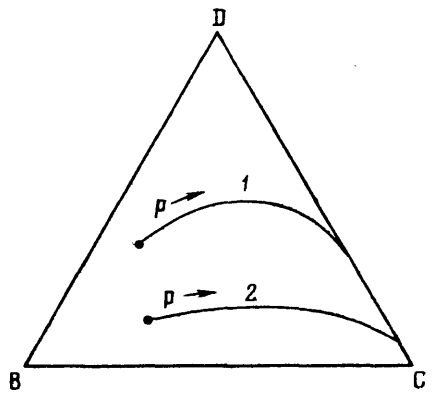


Figure 6. The mole fractions of the functional groups which failed to react in the copolycondensation of terephthalic acid dichloride (A) with dian (B), tetrachlorodian (C), and phenolphthalein (D) at 220°C in solution in α-chloronaphthalene. Curves *1* and *2* correspond to different initial conditions.

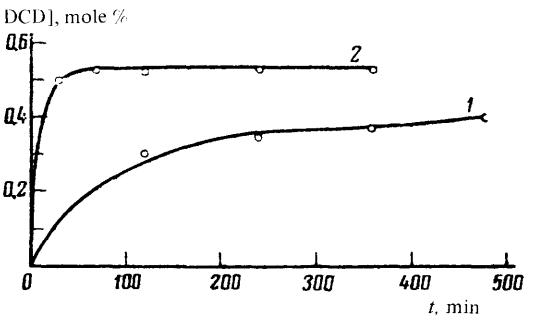


Figure 7. Dependence of the content of dichlorodian (DCD) in the 0.5 : 0.5 : 1 copolymer of dichlorodian, phenolphthalein, and terephthalic acid dichloride on the reaction time; reaction temperature (°C): 1) 180; 2) 242 (isokinetic temperature).

Data indicating the inhomogeneity of the compositions of the copolyesters synthesised from terephthalic acid dichloride, bisnaphthol, and dian were obtained by fractionation and by plotting integral and differential MWD curves for the copolymers. According to theoretical studies [75,76], fractionation of copolymers does not yield an exact characteristic of either the inhomogeneity of the

macromolecules with respect to size or of the inhomogeneity of their chemical composition. However, it follows from these studies that it is possible to select a system in which fractionation is based solely on the molecular weight of the macromolecules. Fractionation in the system where the result obtained is influenced by another parameter (chemical composition) nevertheless does not permit the elimination of the influence of the first parameter. Thus, although it is impossible to determine the distribution function with respect to composition by fractional precipitation, one can observe the chemical inhomogeneity of copolymers if different results are obtained in different systems. It has been found that the solvent (chloroform + ethanol)–precipitant (ethylene glycol) system is relatively insensitive to the chemical composition of the copolymer investigated. This factor enables us to obtain fractions with virtually identical compositions and to plot MWD curves having the shape typical of polycondensation polymers. The same samples, fractionated in a solvent (tetrachloroethane + phenol)–precipitant (n-heptane) system, give rise to fractions differing in chemical composition, and the MWD curves differ appreciably from those obtained previously.

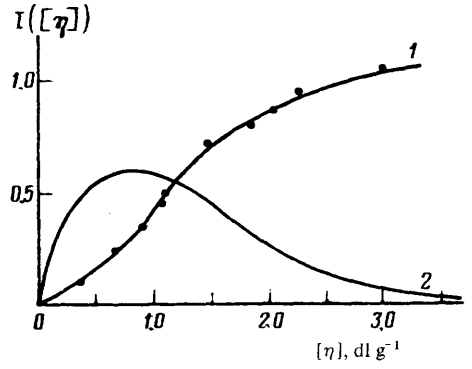


Figure 8. Isokinetic (curve *1*) and differential (curve *2*) MWD curves for the copolyarylate of terephthalic acid dichloride, dian, and bisnaphthol obtained by fractionation in the chloroform + ethanol (5 : 1 by weight)–ethylene glycol system at 25°C.

Figs. 8 and 9 also illustrate MWD curves for both systems, whose comparison leads to the conclusion that the polycondensation copolymers are chemically inhomogeneous.

Thus the experimental data suggest that, when there are differences between the reactivities of the comonomers, the more reactive comonomer is comparatively rapidly exhausted, while the gradual disappearance of the less reactive monomer continues up to high degrees of reaction.

We believe that the consecutive introduction of comonomers into the reaction should be reflected in the microstructure of the macromolecules of the copolycondensate. Similarly, if the reactivities of the two comonomers are the same or almost the same and the composition of the copolymer remains constant regardless of the degree of reaction, the microstructure of the macromolecules must be affected.

Consequently a new problem arises—that of the selection of a system in which both comonomers would have the same activity. It can be solved theoretically fairly readily. It is known[77,78] that the temperature dependence of the reactivity of the terminal groups during high-temperature condensation obeys the Arrhenius equation. If a polycondensation reaction between functional groups A and B take place in the system, then the temperature dependence of the reaction rate constant is

$$\ln k_{AB} = D_{AB} - \frac{E_{AB}}{RT}, \qquad (17)$$

or, for a reaction between functional groups A and C:

$$\ln k_{AC} = D_{AC} - \frac{E_{AC}}{RT}, \qquad (18)$$

where D_{AB}, D_{AC}, E_{AB}, and E_{AC} are constants characteristic of the corresponding polycondensation reactions, T is the temperature (K), and R the gas constant.

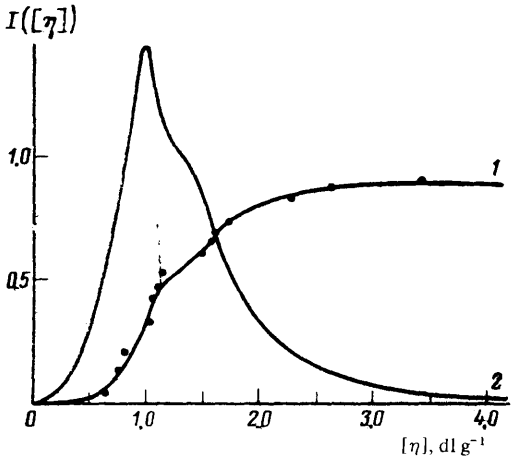


Figure 9. Integral (curve *1*) and differential (curve *2*) MWD curves for the copolyarylate of terephthalic acid dichloride, dian, and bisnaphthol obtained by fractionation in the phenol + tetrachloroethane (1 : 3 by weight)–*n*-heptane system at 25°C.

The reactivities of the comonomers B and C in their reaction with the intermonomer A are equal, whereupon $k_{AB} = k_{AC}$. This happens at a temperature which is called the isokinetic temperature (T_{is}):

$$T_{is} = \frac{E_{AC} - E_{AB}}{R(D_{AC} - D_{AB})}. \qquad (19)$$

At any instant during the copolycondensation process, carried out at the isokinetic temperature, the concentrations of the functional groups of the two comonomers B and C which have not reacted are proportional to the initial concentrations c^0_B and c^0_C. The probabilities of the reaction of both functional groups at any instant are therefore identical and equal to the mole fractions of the given comonomers in the mixture of monomers; consequently, the structures of macromolecular chains formed at the isokinetic temperature should be statistical.

However, the existence of the isokinetic temperature does not alone imply that reaction can be carried out at this temperature. For high-temperature copolycondensation in solution, the range of temperatures suitable for reaction is only a few tens of degrees. On the one hand, this range is restricted by the low rates of both reactions at low temperatures and, on the other, by the thermal instability of the monomers in the solvent above 200°C. However, Turska et al.[79] found that there exist monomer systems whose isokinetic temperature is in the range accessible to study. They determined T_{is} graphically using the Arrhenius coordinates $\lg k = f(1/T)$. The point of intersection of the experimental straight lines corresponds on the abscissa axis to a quantity which is the reciprocal of the isokinetic temperature (Fig. 10). Table 2 lists the isokinetic temperatures found by Turska and coworkers.

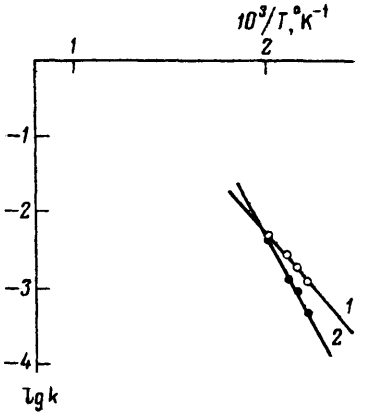
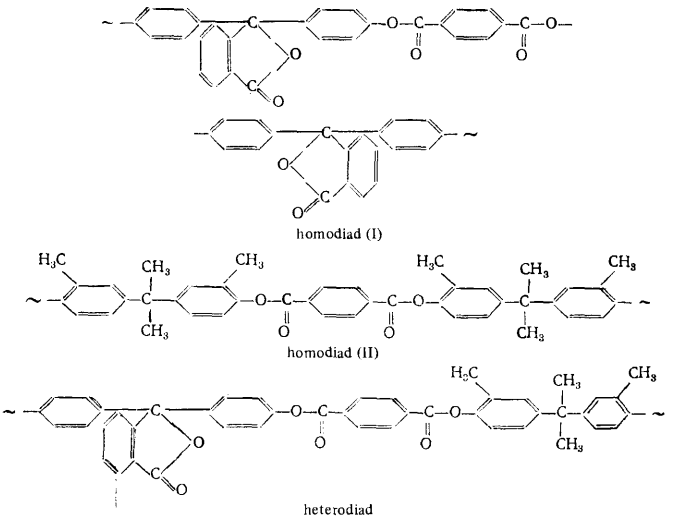


Figure 10. Graphical determination of the isokinetic temperatures for dian (line *1*) and dimethyldian (line *2*) in the reaction with terephthalic acid dichloride in α-chloronaphthalene.

Table 2. The isokinetic temperatures for the copolycondensation of the comonomer systems investigated (the intermonomer is terephthalic acid dichloride).

Comonomers		T_{is}, °C
B	C	
Dian	Phenolphthalein	155
Dian	Dimethyldian	229
Dian	Tetramethyldian	341
Dian	Dinitrodian	366
Dian	Dichlorodian	355
Dian	Tetrachlorodian	340
Phenolphthalein	Dimethyldian	200
Phenolphthalein	Dinitrodian	307
Phenolphthalein	Dichlorodian	242
Phenolphthalein	Tetramethyldian	280
Phenolphthalein	Tetrachlorodian	287

As an example, we shall consider one such system, consisting of terephthalic acid dichloride (the intermonomer A), dimethyldian, and phenolphthalein (the comonomers B and C). It was established by thin-layer chromatography, infrared spectroscopy, and elemental analysis of the reaction products that, when the process is carried out at T_{is} = 200°C, the composition of the copolymer hardly changes with the degree of reaction. The microstructure of the copolymer was studied by high-resolution ^{1}H NMR, whereby the contents of the homo- and hetero-diads in the macromolecules were determined:



Preliminary studies showed that the signal of the phenylene protons of the terephthalic acid residue in the ^{1}H NMR spectra of the polyesters investigated is a singlet (δ = 8.4 p.p.m.). In order to resolve this signal into individual components due to homo- and hetero-diads, tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-3,5-dioneeuropium [Eu(fod)$_3$] was used as an additive. Fig. 11 shows that, in the presence of Eu(fod)$_3$, it is possible to distinguish clearly signals in the ^{1}H NMR spectrum corresponding to the chemical shifts of the phenylene protons of the intermonomer in the homo- and hetero-diads.

The constancy of the composition of the copolycondensate synthesised at the isokinetic temperature, observed by other methods, was confirmed by ^{1}H NMR. Use was made for this purpose of Eqn. (5) quoted above. The values of K_M determined by ^{1}H NMR for copolymers synthesised at the isokinetic temperature (with a high accuracy) proved to be unity, which corresponds to a statistical distribution of units in their macromolecules. This result confirms the validity of our theoretical considerations.

The problem of the nature of the copolycondensation process at temperatures fairly different from the isokinetic temperature is no less interesting. For the above system of monomers, a study was made of the composition and structure of the copolymers obtained at 180° and 220°C, i.e. at temperatures above and below T_{is}. At a temperature different from T_{is} the reactivities of the comonomers are different and, when, for example, $k_{AB} > k_{AC}$, the monomer B reacts faster and the macromolecules of the oligomers and polymers in which it predominates are formed faster and in greater amounts. The concentration of the functional groups of the comonomer B decreases very rapidly almost up to complete exhaustion, after which new molecules are formed in which the comonomer C predominates or molecules where chains containing mainly the less active comonomer C join onto the chains

already formed and begin to grow. Depending on the degree of reaction for which the process is terminated, copolymers are obtained with different degrees of structural inhomogeneity, but there is always a tendency towards a block structure. One may expect the formation in the macromolecule of internal blocks of the more reactive comonomer, while the ends of the chains should contain primarily the less reactive comonomer. For very high degrees of reaction, the interactions between the macromolecules should lead to the formation of multiblock copolymers with different internal blocks, but always with the less reactive comonomers at the ends of the chain.

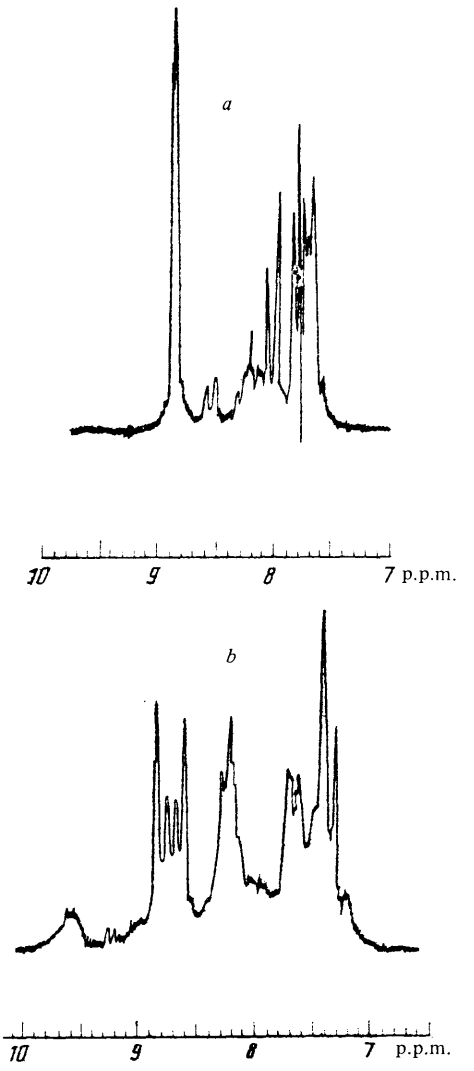


Figure 11. ^{1}H NMR spectrum of the copolyester of terephthalic acid dichloride, dian, and phenolphthalein: *a*) without Eu(fod)$_3$; *b*) with added Eu(fod)$_3$.

In order to confirm the validity of this reasoning, the composition of the copolymer was determined in the course of the reaction. In conformity with earlier considerations, above the isokinetic temperature (220°C) the more reactive comonomer proved to be dimethyldian, which disappeared faster from the reaction mixture, while phenolphthalein, the less reactive comonomer failed to react for a long time. Below the isokinetic temperature (180°C), phenolphthalein proved to be more reactive and dimethyldian failed to react for a long time. The study of the microstructure of the copolymers by ^{1}H NMR using Eu(fod)$_3$ showed that the coefficient of microheterogeneity of the copolymers is $K_M = 0.87$ in both cases.

The difference between the numerical values of K_M for the copolymers obtained at the isokinetic or another temperature indicates a difference between the microstructures of their molecules. The values of the parameter K_M show that copolymers with a completely random statistical chain structure are formed at the isokinetic temperature, while at a non-isokinetic temperature there is a tendency towards the formation of block structures. One should take into account the fact that, for high degrees of reaction, the synthesis of copolymers at isokinetic and non-isokinetic temperatures should lead to the formation of products of the same compositions but with a different structure of macromolecular chains.

oOo

The present review of studies in the field of copolycondensation permits the conclusion that there is as yet no generally recognised equation giving a complete description of the observed phenomena. One should also note that no attempts have been made at an experimental confirmation of the results of the majority of very interesting theoretical studies. Although one should bear in mind that a satisfactory agreement between experiment and theory does not alone demonstrate the validity of the theory, nevertheless the assumptions made in the development of the theory can then be regarded as admissable.

The reason for the discrepancies between different workers' views is apparently the lack of justification of the attempts to describe extremely varied copolycondensation processes in terms of a single theory. It may be that hypotheses which are correct for one group of processes are inadmissible for another. The introduction of limitations as regards the applicability of the theoretical ideas which have been developed should reduce to a large extent the discrepancies in this field. Studies dealing with definite groups of processes hardly involve contradictions under these conditions and in addition permit more general conclusions in many instances. These may include the demonstration of a significant influence of temperature on high-temperature copolycondensation in solution, where even a slight change of temperature in the region of T_{is} may alter the macromolecular structure. Consequently, instead of being a purely kinetic parameter, temperature becomes a parameter which influences the composition and structure of copolymers. Presumably this conclusion is valid also for other groups of copolycondensation processes.

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Block Copolymers of the Polycondensation Type

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A new class of block copolymers. namely block copolymers of the polycondensation type, is considered. A general indication of the methods of synthesis and structures of such block copolymers is given and the available information about different examples of block copolymers of the polycondensation type is surveyed.
The bibliography includes 174 references.

CONTENTS

I. Introduction 42
II. Methods of synthesis and structure of block copolymers of the polycondensation type 42
III. One-type block copolymers 47
IV. Two-type block copolymers 49
V. Three- and multi-type block copolymers 58

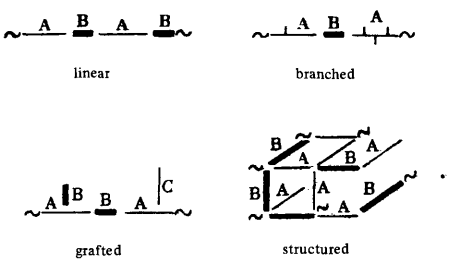
I. INTRODUCTION

The majority of the block copolymers known at this present time have been obtained by polymerisation methods [1-6], but in recent years an increasing number of studies have been devoted to block copolymers synthesised with the aid of polycondensation processes [7,8].

A separate examination of block copolymers of the polycondensation type merits attention for a number of reasons. 1. Virtually any homopolymer, of either polymerisation or polycondensation type, may be used as the corresponding oligomer with terminal functional groups in polycondensation reactions leading to the formation of block copolymers. The synthesis by polymerisation methods of oligomers having terminal functional groups capable of condensation is much simpler and technologically more effective than the synthesis by polycondensation methods of oligomers having terminal functional groups capable of polymerisation. Thus the synthesis of oligomers of the first type leads to considerable possibilities, realisable in practice, for the synthesis of block copolymers containing simultaneously polymer blocks of the polymerisation and polycondensation types. 2. In contrast to block copolymers of the polymerisation type, block copolymers of the polycondensation type can contain blocks of a wide variety of different kinds: aliphatic and aromatic, flexible and rigid, hydrophilic and hydrophobic, unsaturated and saturated, organic and inorganic, etc. 3. In most instances block copolymers of the polycondensation type are multiblock copolymers with a controllable length of blocks, whereas block copolymers of the polymerisation type are mainly two- and three-block copolymers with a poorly controllable length of blocks. The transition to the multiblock structure of block copolymers in which microphase separation occurs is accompanied by the formation of a more perfect physical network owing to the formation of a large number of domains consisting of highly fusible blocks, their more uniform distribution throughout the bulk of the polymer, and the involvement of the same macromolecule in the construction of a large number of domains. The controllable length of blocks permits the development of a stable technological manufacturing process for block copolymers. 4. Finally, perhaps the most significant factor is the successful development, to a large extent owing to the studies by V.V.Korshak and his school, of the theory of irreversible (non-equilibrium) polycondensation [9], which laid extensive foundations for the synthesis of block polymers of the polycondensation type. This refers primarily to acceptor-catalytic polycondensation, the mild conditions for the occurrence of which permit the synthesis of block copolymers with virtually complete suppression of the exchange processes and also lead to the possibility of the formation of block copolymers directly from the monomers [10,11].

II. METHODS OF SYNTHESIS AND STRUCTURE OF BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

Block copolymers of the polycondensation type include block copolymers the last stage in the formation of which is a polycondensation reaction. Such copolymers can be linear, branched, grafted (graft block copolymers), and structured:



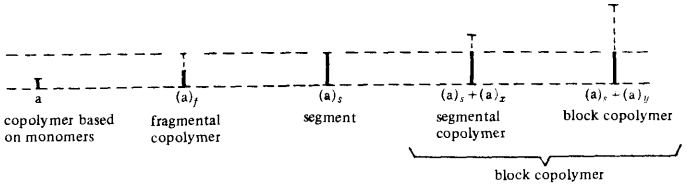
Linear block copolymers, to the consideration of which the present review is devoted, have been most thoroughly investigated at the present time.

Linear block copolymers are copolymers whose macromolecules consist of alternating blocks of homopolymers or statistical copolymers differing in composition or structure [12]. The concept of the "block" implies a relatively long sequence of elementary units of the polymer, whose length is equal to or greater than the length of the macromolecular segment which is a statistical element of the hypothetical polymer chain adequately simulating the physical properties of the macromolecule [13]. For this reason, terms such as "segmented (segmental) copolymers" and "block copolymers" are used simultaneously in the literature. The first term is frequently applied to segmented polyurethanes [12-15], where the molecular weights of the blocks do not exceed several thousand.

These are short-block copolymers, so that the number of blocks in their macromolecules is considerable. The second term, "block copolymers", is more applicable to long-block copolymers. The molecular weights of the constituent blocks in such copolymers can range from several to tens of thousands. The number of blocks in the macromolecules of polymers of this kind may vary from two (the minimum value for block copolymers) to several tens. Evidently, when the lengths of the blocks in the copolymer are similar to the length of the geometrical segment of the macromolecule, the terms "segmental copolymer" and "block copolymer" become synonymous.

Copolymers containing sequences of elementary units whose length is less than that of the geometrical segment of the macromolecule cannot be regarded as block copolymers; they can be called fragmental copolymers. These copolymers are formed when bifunctional fragmental compounds, consisting of more than one repeating elementary unit and whose chain length is less than that of the segment, are used. The introduction of such a compound into the copolymer macromolecule is equivalent to the introduction into the latter of a chain fragment of another polymer. However, in contrast to blocks, the fragments impart to the new polymer an insignificant proportion of the properties characteristic of their high-molecular-weight homologue.

Bearing in mind the foregoing considerations, the hierarchy of linear copolymers can be represented as follows as a function of the length of the sequences of elementary units incorporated in the macromolecule:



Here a is the elementary unit and f, s, x, and y are the numbers of elementary units ($f < s$ and $x \leqslant y$).

Taking into account the fact that the block length should not be smaller than the length of the segment, the structure of block copolymers can be described by terms such as segment-monomeric, segment-fragmental, segment(1)–segment(2)-al, etc. copolymers (Table 1). These names enumerate initially the polymeric segments with structures (1), (2), etc. in the copolymer macromolecule and indicate the nature of the chain-lengthening agent (if one is used), whereby the segments are chemically combined in the macromolecule.

We shall examine the definitions of certain characteristics of the block copolymers presented in Table 1. A component is a block of a homopolymer or a copolymer having a definite composition and structure incorporated in the block copolymer. "Componentality" is the number of blocks of different composition and structure constituting the macromolecules of the block copolymer. One-component block copolymers contain blocks of a single chemical kind connected via the residues of the chain-lengthening agent; the molecules of two-component block copolymers include blocks with two different structures, which may differ by the presence of other substituents or by the steric structure of the chain, etc. The type composition of a block copolymer (it can be a one-type, two-type, three-type, and multitype copolymer) is a quantity equal to the number of types of macromolecular compounds incorporated in the form of chemically combined oligomeric analogues (blocks) in the macromolecule of the block copolymer. "Blockability" is the total number of blocks of any kind in the macromolecule of the block copolymer. The minimum number of blocks which can be observed in long-block copolymers is two and the maximum number is determined by the length of the constituent blocks and the length of the macromolecule of the block copolymer itself and can amount to several tens. In terms of the regularity of the alternation of blocks along the macrochain, block copolymers of the polycondensation type can be divided into regularly alternating and irregularly alternating. This characteristic of block copolymers refers to their fine structure (microstructure) and its determination, particularly for irregularly alternating block copolymers, is as yet difficult.

Table 1. Characteristics of block copolymers.

Structure of copolymer	No. of components ('componentality')	No. of blocks ('blockality')	No. of types	Regularity in alternation of blocks
Segment-monomeric	1	two-, three-, and multi-block	1	regularly and irregularly alternating
Segment-fragmental	1	two-, three-, and multi-block	1	ditto
Segment-fragment-monomeric	1	three- and multi-block	1	ditto
Segment (1)-segment(2)-al	2	two-, three-, and multi-block	1 and 2	regularly alternating
Segment(1)-segment(2)-monomeric	2	two-, three- and multi-block	1 and 2	regularly and irregularly alternating
Segment(1)-segment(2)-fragmental	2	two-, three-, and multi-block	1 and 2	ditto
Segment(1)-segment(2)-segment(3)-al	3	three- and multi-block	1,2 and 3	ditto
Segment(1)-segment(2)-segment(3)-monomeric, etc.	3 (multi-component)	three- and multi-block > 3 (multiblock)	1,2 and 3 ⩾ 1	ditto

The chemical structure of polymers can be treated at two different levels: at the levels of the macrostructure and the microstructure. The macrostructure of the polymer is characterised by parameters of the following kind:

I. The chemical structure of the elementary unit of the polymer (idealised formula which does not reflect all the characteristics of the polymer chain structure).

II. The average chemical (elemental) composition of the polymer.

III. The average molecular weight of the polymer. The knowledge of the macrostructure of the polymer is usually sufficient to achieve a comparative characterisation of different polymers, but the macrostructure cannot explain the whole series of features of the physical and chemical properties of high-molecular-weight compounds. In such instances a more detailed study of polymers, yielding information about their microstructure, is necessary.

The concept of the microstructure of the polymer is much more profound than the concept of its macrostructure and includes a much greater number of parameters characterising the structure of the polymeric compound [16-20]; these parameters are listed below:

I. The chemical structures of the main and "anomalous" [18,19] elementary units in the chain (the heterounit property of polymers), terminal blocks, units, and terminal functional groups.

II. Chemical inhomogeneity:

1. Inhomogeneity with respect to molecular weight.

2. Inhomogeneity with respect to chemical composition (compositions inhomogeneity).

3. Inhomogeneity with respect to chemical structure [18, 19]: (a) inhomogeneity with respect to the degree of branching (number of branching points, chemical structure, and length of branches); (b) inhomogeneity in the "head-to-head" and "head-to-tail" combinations of units; (c) inhomogeneity as regards the presence of isomeric units; (d) inhomogeneity with respect to microtacticity (owing to the differences in the configurations of the asymmetric carbon atoms making up the macromolecular chain); (e) inhomogeneity of macromolecules induced by the presence of anomalous units owing to incomplete trimerisation, incomplete formation of the carbo- or hetero-cycle in the polycyclisation or polycyclocondensation reaction, copolymerisation and copolycondensation, and chemical reactions of the units in the macromolecules.

4. Inhomogeneity with respect to the chemical nature of the terminal blocks, units, and functional groups.

III. Inhomogeneity in the distribution of the main and anomalous units and sections of different chemical compositional structure in the macrochain.

One should note that, whereas the method for the determination of the macrostructure of the polymer has now been thoroughly developed and presents no difficulty, the determination of its microstructure is difficult even for simple polymeric systems. This problem becomes still more complex on passing from homopolymers to copolymers and block copolymers [17,20].

Nevertheless, even without experimental data for the microstructure of block copolymers of the polycondensation type, one can assume that these block copolymers will exhibit an appreciable inhomogeneity, i.e. a difference between the macromolecules of the same specimen of the block copolymer.

We shall now consider in a general form certain kinds of block copolymers of the polycondensation type and methods for their synthesis.

A. ONE-COMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

One-component block copolymers are at the same time one-type block copolymers and can have a two-, three-, and multi-block structure (Table 1). One-component two-block copolymers can be obtained by the interaction of an excess of the oligomer having terminal functional groups f with a monomeric or fragmental chain lengthening agent (cl):

$$2\ \mathrm{f{-}A{-}f} + \mathrm{f'{-}cl{-}f'} \rightarrow \mathrm{f{-}A{-}cl{-}A{-}f}\ . \qquad (1)$$

One-component three-block copolymers can also be obtained from the same initial compounds as two-block copolymers, but in this case two stages are required; the low-molecular-weight compound can behave under these conditions as a functional group substituting agent (fgs) (monomeric or fragmental) in the oligomer rather than a chain lengthening agent:

$$\mathrm{f{-}A{-}f} + 2\mathrm{f'{-}fgs{-}f'} \xrightarrow{(a)} \mathrm{f'{-}fgs{-}A{-}fgs{-}f'}\ ;$$
$$\mathrm{f'{-}fgs{-}A{-}fgs{-}f'} + 2\mathrm{f{-}A{-}f} \xrightarrow{(b)} \mathrm{f{-}A{-}fgs{-}A{-}fgs{-}A{-}f}\ . \qquad (2)$$

Thus the functional group substituting agent is a low-molecular-weight compound used to substitute one set of functional groups in oligomers and polymers by another, whereby block copolymers having a specified structure can be synthesised. Functional group substituting agents can be divided into those whose residues are incorporated in the macromolecule of the block copolymer (monomeric and fragmental substituting agents) and substituting agents which are not incorporated in the macromolecule of the block copolymer (H_2O, $POCl_3$, etc.).

One-component multiblock copolymers are formed when equimolar amounts of a bifunctional oligomer react with a single chain lengthening agent:

$$n\,\mathrm{f{-}A{-}f} + n\,\mathrm{f'{-}cl{-}f'} \rightarrow \mathrm{f{-}[{-}A{-}cl{-}]_n{-}f'} \qquad (3)$$

or simultaneously with several chain lengthening agents of different chemical types. In the latter case one may speak of a regular or irregular alternation of lengthening agents of different kinds along the macrochain of the block copolymer.

Before the synthesis of a multiblock block copolymer, the initial oligomers may be subjected to interaction with a rigorously stoichiometric or an excess amount of functional group substituting agents in order to replace functional groups inactive with respect to the chosen chain lengthening agent by active groups:

$$n\,\mathrm{f''{-}A{-}f''} + 2n\,\mathrm{f{-}fgs{-}f} \xrightarrow{(a)} n\,\mathrm{f{-}fgs{-}A{-}fgs{-}f}\ ; \qquad (4)$$
$$n\,\mathrm{f{-}fgs{-}A{-}fgs{-}f} + n\,\mathrm{f'{-}cl{-}f'} \xrightarrow{(b)} \mathrm{f{-}[{-}fgs{-}A{-}fgs{-}cl{-}]_n{-}f'}\ .$$

Among one-component multiblock block copolymers, one can distinguish block copolymers with constant block lengths:

$$\sim\!\!\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\mathrm{cl}\overset{A}{\text{—}}\sim$$

and variable block lengths (varied, for example, by one of several chain lengthening agents, which do not yield an anomalous unit on combination of two oligomers):

$$\sim\!\!\overset{A}{\text{—}}\mathrm{cl}_2\overset{A(A+A+A)}{\text{———}}\mathrm{cl}_3\overset{A}{\text{—}}\mathrm{cl}_3\overset{A(A+A)}{\text{———}}\mathrm{cl}_2\overset{A}{\text{—}}\sim\ .$$

All the polymers containing anomalous units in their macromolecules can be regarded as the latter variety of block copolymers.

B. TWO-COMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

Since most attention is being devoted nowadays to the synthesis and the study of the properties of block copolymers of this kind, we shall consider them in greater detail. Two-component two-block copolymers of type A–B may be obtained by the interaction of two polymers, each containing at the ends of its macrochains one functional group capable of polycondensation, and by the interaction of a stoichiometric amount of a chain lengthening agent with an equimolar amount of two polymers whose molecules each contain one functional group at the end of the chain:

$$\mathrm{A{-}f} + \mathrm{f'{-}cl{-}f'} + \mathrm{f{-}B} \rightarrow \mathrm{A{-}cl{-}B}\ . \qquad (5)$$

The polymers A–f and f–B, which differ in their composition or structure, may belong either to polymers of one type (a polyether, a polyamide, etc.) or to two different types of polymers (a polycarbonate and a polyorganosiloxane, a polyester and a polyether, etc.).

Two-component three-block block copolymers with A–B–A and B–A–B block sequences can be obtained by the interaction of a bifunctional oligomer B or A with an excess of the oligomer A or B respectively:

$$\geqslant 2f-A-f+f'-B-f' \rightarrow f-A-B-A-f \quad . \qquad (6)$$

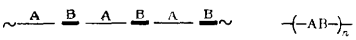
If one of the initial oligomers contains only one functional group at the end of the chain, the synthesis of the three-block copolymer is simplified:

$$2\,A-f+f'-B-f' \rightarrow A-B-A \quad . \qquad (7)$$

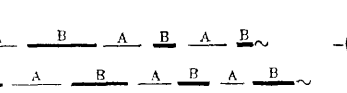
Two-component multiblock copolymers of the polycondensation type may be regularly alternating or irregularly alternating (regular and irregular).

1. Regularly Alternating Block Copolymers

Regularly alternating block copolymers are multiblock copolymers with a regular alternation of blocks of different kinds along the macrochain. Among the block copolymers of this kind, one should distinguish regularly alternating block copolymers with constant block lengths (within the limits of the polydispersity with which the initial oligomers having the specified molecular weight have been obtained):



and regularly alternating block copolymers with varying block lengths (one or both):



In view of the different types of behaviour under certain conditions of blocks of the same kind but different lengths, the block copolymers $-(-AB-)_n-$, $-(-A'B-)_n-$, $-(-AB'-)_n-$, and $-(-A'B'-)_n-$ will apparently exhibit different properties.

Regularly alternating two-component multiblock copolymers can be obtained in one stage when the initial oligomers have terminal functional groups of different types which interact with one another:

$$3n\,f-A-f+3n\,f'-B-f' \rightarrow f'-B-(-A-B-)_n-f'+$$
$$+f-(-A-B-)_n-A-f+f'-B-(-A-B-)_{n-2}-A-f \quad . \qquad (8)$$

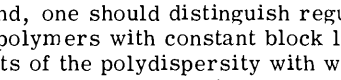
On the other hand, if the initial oligomers have terminal functional groups of the same type which do not interact with one another, regularly alternating block copolymers are formed in two stages and it is necessary to use a functional group substituting agent. Compared with the previous case, a wider spectrum of different block copolymer macromolecules is formed, the copolymers differing from one another in the nature of the terminal blocks, units, and functional groups:

$$10n\,f-A-f+20n\,f'-fgs-f' \xrightarrow{(a)} 10n\,f'-fgs-A-fgs-f' \xrightarrow{(b)}$$
$$\xrightarrow{+10n\,f-B-f} f-B-(-fgs-A-fgs-B-)_n-f+$$
$$+f-(-A-fgs-B-fgs-)_n-A-f+f-B-(-fgs-A-fgs-B-)_{n-2}-$$
$$-fgs-A-f+f'-fgs-B-(-fgs-A-fgs-B-)_n-f+$$
$$+f'-fgs-B-(-fgs-A-fgs-B-)_n-fgs-f'+ \qquad (9)$$
$$+f'-fgs-(-A-fgs-B-fgs-)_n-A-f+$$
$$+f'-fgs-(-A-fgs-B-fgs-)_n-A-fgs-f'+$$
$$+f'-fgs-B-(-fgs-A-fgs-B-)_{n-2}-fgs-A-f+$$
$$+f-B-(-fgs-A-fgs-B-)_{n-1}-fgs-A-fgs-f'+$$
$$+f'-fgs-B-(-fgs-A-fgs-B-)_{n-2}-fgs-A-f$$

Thus the macromolecules of two-component regularly alternating multiblock copolymers of the polycondensation type differ from one another by the molecular weight of both the macromolecules themselves and their constituent blocks, by their chemical composition and structure, by the inhomogeneity in the distribution of the main and anomalous units along the chain (blocks and the macromolecules), and by the nature of the terminal blocks, units, and functional groups.

2. Irregularly Alternating Block Copolymers

Irregularly alternating block copolymers are multiblock copolymers with an irregular alternation of blocks of different kinds. Among block copolymers of this type, one should distinguish irregularly alternating block copolymers with constant block lengths (within the limits of the polydispersity with which the original oligomers having a specified molecular weight have been obtained):



and irregularly alternating block copolymers with varying (for example on increasing the length of block B without the appearance of an anomalous unit) lengths of the blocks (one or both):



(The subscripts $\underline{n}$ and $\underline{m}$ denote an irregular distribution of blocks A and B along the macrochain.)

Many methods for the synthesis of irregularly alternating two-component block copolymers have now been described; an even greater number appear to be possible in view of the prospects arising from the very principle of the synthesis of these block copolymers. We may formulate these methods of synthesis in an abbreviated form (each component is an individual substance):

ol + m + cl,	ol-1 + ol-2,
ol + m-cl,	ol-1 + ol-2 + cl,
ol + cm + cm-cl,	cm-1 + cm-2,
ol + cm-fgs + cm-cl,	

where ol is a bifunctional oligomer, m a monomer (a substance capable of homopolycondensation), m-cl a substance behaving simultaneously as a monomer and a chain lengthening agent, cm a comonomer (a substance incapable of homopolycondensation), cm-cl a substance behaving as a comonomer and a chain lengthening agent (for example, a diol in the synthesis of polyurethanes), and cm-fgs a substance behaving simultaneously as a monomer and a functional group substituting agent (for example, di-isocyanate in one of the methods for the synthesis of polyurethanes).

We shall now consider block copolymers obtained by two of the most frequently used methods for the synthesis of irregular block copolymers.

(a) Irregular (ol-1 + ol-2 + cl) two-component multiblock copolymers. Such block copolymers are formed when the initial oligomers with

terminal groups of the same type which do not interact with one another are combined into a common macrochain in a single stage with the aid of a chain lengthening agent:

$$\begin{aligned} &zn\,f{-}A{-}f + zm\,f{-}B{-}f + z(n+m)\,f'{-}cl\ {-}f' \rightarrow \\ &\rightarrow f{-}A{-}cl\ {-}\{{-}[{-}A{-}cl\ {-}]_{\underline{n}}{-}[{-}B{-}cl\ {-}]_{\underline{m}}{-}\}_z{-}A{-}f + \\ &+ f'{-}cl\ {-}A{-}cl\ {-}\{{-}[{-}A{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl{-}]_{\underline{m}}{-}\}_z{-}A{-}cl{-}f' + \\ &+ f'{-}cl\ {-}A{-}cl\ {-}\{{-}[{-}A{-}cl\ {-}]_{\underline{n}}{-}[{-}B{-}cl\ {-}]_{\underline{m}}{-}\}_z{-}A{-}f + \text{etc.} \end{aligned} \quad (10)$$

In all, there is a possibility of ten combinations of terminal blocks, units, and functional groups:

A ~ A; cl–A ~ A–cl; cl–A ~ A;
B ~ B; cl–A ~ B–cl; cl–B ~ B;
A ~ B; cl–A ~ B–cl; cl–A ~ B; A ~ B–cl.

The macromolecules of irregular (ol-1 + ol-2 + cl) two-component multiblock copolymers of the polycondensation type differ from one another by the molecular weights of both the macromolecules themselves and their constituent blocks, by the chemical composition (determined mainly by the molecular weight and numbers of blocks of different kinds) and chemical structure, by the inhomogeneity in the distribution of the main and anomalous units along the chain (blocks and macromolecules), by the inhomogeneity in the distribution of blocks of different chemical composition or structure along the macrochain, and by the nature of terminal blocks, units, and functional groups [Eqn.(10)].

The examples quoted show that the chain lengthening agent is a low-molecular-weight compound (monomeric or fragmental) which is capable of reacting with oligomers or low-molecular-weight polymers having terminal functional groups and thereby lengthening the polymer chain. Furthermore, compounds which interact simultaneously with the initial oligomer and with the low-molecular-weight compound, intended for the synthesis of a non-oligomeric block, also behave as chain lengthening agents. Depending on the chemical structure of the initial oligomer, the chain lengthening agent can be of the same kind (its residue is present in the oligomer chain) or "alien" in relation to the oligomer (the oligomer does not contain residues of this kind). If the chain lengthening agent is used to synthesise at least one of the initial oligomers, then the molecular weight of blocks of different chemical composition or structure is related not only to the numbers of blocks A or B in a single macrochain but also to their length, which may differ from the length of the initial oligomers (an irregularly alternating block copolymer with varying block lengths). If the chain lengthening agent is of an "alien" type, then the overall molecular weight of blocks of the same kind will be determined by their number in the macromolecule.

The number of blocks A and B in the macrochain is a statistical quantity and depends on the length of the entire macrochain, on the conditions for the synthesis of the block copolymer, on the relative reactivities of the terminal functional groups of the oligomers, and on the nature of the chain lengthening agent. Precisely in the case of a homogeneous chain lengthening agent the number of the corresponding (related) blocks, for example A, may be greatly reduced owing to the increase in their length without the appearance of heterounits. In the case of an "alien" chain lengthening agent, each block of the macrochain, including blocks of the same nature, is separated from others by an anomalous unit. In this situation the number of blocks A or B in a single macrochain is therefore determined by the number of oligomers f–A–f or f–B–f used to form the macrochain.

(b) Irregular (ol + cm + cm-cl) two-component multiblock copolymers. Such block copolymers are formed in a single stage from the initial oligomer, for example, f–B–f, and the monomer f–A–f or f″–A–f″ with the same functional groups as in the oligomer or others which are also capable of reacting with a chain lengthening agent:

$$\begin{aligned} &zn\,f{-}a{-}f + zm\,f{-}B{-}f + z(n+m)\,f'{-}cl{-}f' \rightarrow \\ &\rightarrow f{-}\{{-}[{-}a{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl{-}]_{\underline{m}}{-}\}_z{-}a{-}f + \\ &+ f'{-}cl\ {-}\{{-}[{-}a{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl{-}]_{\underline{m}}{-}\}_z{-}a{-}cl\ {-}f' + \\ &+ f{-}\{{-}[{-}a{-}cl{-}]_{\underline{n}}{-}[{-}B{-}cl\ {-}]_{\underline{m}}{-}\}_z{-}a{-}cl{-}f' + \text{etc.}; \end{aligned} \quad (11)$$

In all, there is a possibility of 21 combinations of terminal blocks, units, and functional groups.

In this case [Eqn.(11)] the molecular weight of blocks A = $-(-a-cl-)_n-$ in individual macromolecules is determined not only by the number of these blocks but also by their length. Variations in the length of blocks A in irregular (ol + cm + cm-cl) block copolymers may be more numerous than in the case of irregular (ol-1 + ol-2 + cl) block copolymers.

The considerations described in relation to two-component block copolymers show that the determination of the complete microstructure of block copolymers of the polycondensation type constitutes an extremely complex and important problem, which still awaits solution. In the present stage the determination of the microstructure of polymers is frequently limited to the determination of the molecular weight distribution and the distribution with respect to chemical composition.

C. THREE-COMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

It is possible to distinguish the following kinds of such block copolymers:

1. Three-component three-block copolymers in which the distribution of blocks of different chemical kinds along the macrochain is of the type A–B–C, A–C–B, or B–A–C.

2. Three-component multiblock copolymers. These block copolymers can be regularly alternating, $-[-A-B-C-]_z-$, $-[-A-C-B-]_z-$, and $-[-B-A-C]_z-$, or irregularly alternating, $-\{-[A-]_n--[-B-]_m--[-C-]_p--\}_z-$, etc. with constant or variable block lengths.

The properties of three-component block copolymers can be greatly influenced by the distribution of different blocks along the copolymer macrochain. Depending on the chemical nature of the constituent blocks and the required structure of the final polymeric product, three-component multiblock copolymers can be synthesised in one or two stages from mono- or bi-functional oligomers and may require the use of different chain lengthening agents and functional group substituting agents. Two-, three-, and multi-block seeds with terminal functional groups can also be used as the initial compounds.

D. MULTICOMPONENT BLOCK COPOLYMERS OF THE POLYCONDENSATION TYPE

It is possible to distinguish the following kinds of such block copolymers:

1. Multicomponent block copolymers in which the number of blocks in the chain is equal to the number of

components or slightly exceeds it, for example, four-component four-block A–B–C–D copolymers, five-component six-block A–B–C–D–E–A copolymers, etc. These block copolymers can have a large number of analogues differing from one another by the distribution of blocks of different chemical types along the macrochain.

2. Multicomponent multiblock copolymers which can be regularly alternating with constant or variable block lengths, $-[-A-B-C-D-E-]_z-$, etc., or irregularly alternating with constant or variable block lengths, namely $-\{-[-A-]_{\underline{n}}-[-B-]_{\underline{m}}-[-C-]_{\underline{p}}-[-D-]_q-\}_z-$, etc.

III. ONE-TYPE BLOCK COPOLYMERS

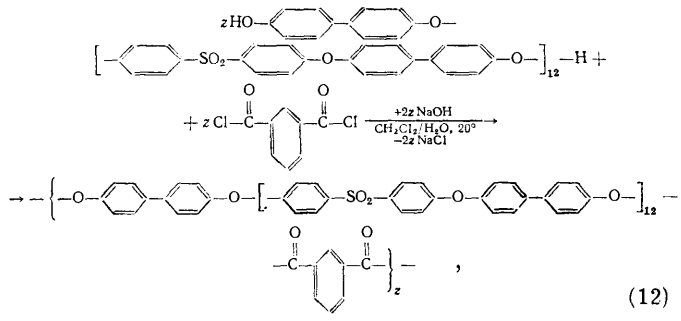
One-type block copolymers of the polycondensation type are copolymers consisting of polymer blocks of the same type which have identical or different compositions. Such block copolymers can be synthesised for the following purposes: (a) to increase the molecular weight of low-molecular-weight polymers having one or two terminal functional groups; (b) to obtain polymers with a uniform distribution of functional groups along the chain; (c) to modify the properties of the polymer by means of residues of the chain lengthening agent (monomeric or fragmental); (d) to modify the properties of the polymer by introducing into its macromolecules blocks of a polymer-analogue differing in its properties.

The increase in the molecular weight of polymers with the aid of a chain lengthening agent may be important in many instances, since many processes yielded only low-molecular-weight polymers are known. In particular, the molecular weight of poly(phenylene oxide) based on 2,6-dimethylphenol may be increased by a factor of two when its sodium salt interacts with di-(4-chlorophenyl) sulphone[23]. The two-block copolymer formed as a result made it possible to obtain stable relatively flexible films.

The low molecular weight of polymers with a system of conjugated multiple bonds greatly impairs their physicomechanical properties and reduces the possibility of obtaining polymeric materials on their basis. The lengthening of the molecules of such low-molecular-weight polymers by means of chain lengthening agents, for example, the poly-Schiff base derived from *p*-phenylenediamine and benzil using a di-isocyanate or a dicarboxylic acid[24], lead, according to Eqn.(1), to the formation of multiblock copolymers with improved physicomechanical properties and effective semiconducting properties.

Block copolymers obtained from oligomers and trifunctional chain lengthening agents (two groups out of three being of the same kind) may be of interest as polymers capable of forming structures with a specified density of the chemical network and also as initial polymers for the synthesis of graft copolymers having a specified frequency of branching points.

The modification of the properties of polymers by the introduction of the residues of a monomeric or fragmental chain lengthening agent, for example, by the interaction of bifunctional oligomers with a chain lengthening agent [Eqn.(1)], is attractive in view of its simplicity: for any bifunctional oligomer intended for subsequent synthesis of two-type block copolymers, it is possible to select a whole series of readily available chain lengthening agents. For example, dihydroxyoligo(arylene sulphone oxides) can react with aromatic[25] and aliphatic[26] dicarboxylic acid dichlorides:



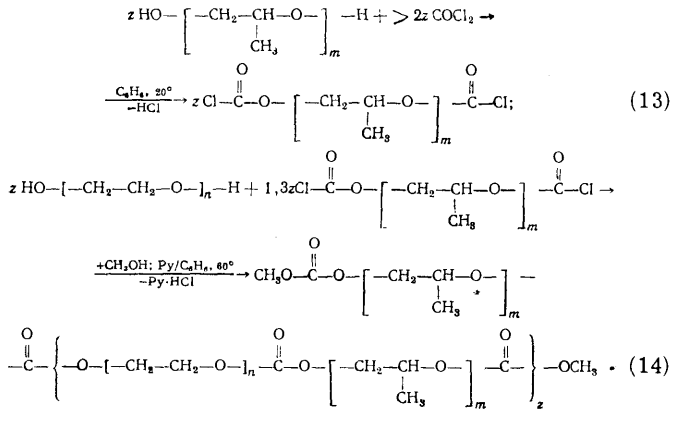
(12)

and with aromatic disulphonyl chlorides[25]. The block copolymers obtained exhibit a high thermal and hydrolytic stability and have useful mechanical and dielectric properties. Segmental-monomeric block copolymers with improved mechanical properties have been obtained from low-molecular-weight polycarbonates having terminal chloroformate groups and diamines, for example, piperazine[27]. Modified polyquinazolinones with improved thermal properties and ready solubility in many solvents have been obtained by the interaction of oligoquinazolinones with terminal amino-groups and pyromellitic dianhydride[28].

In all the examples quoted above one-component block copolymers were described, but the synthesis of two-component one-type block copolymers for which one may expect interesting combinations of the properties of polymer-analogues are of no less interest.

1. Polyether–Polyether Block Copolymers

Regularly alternating multiblock poly(ethylene oxide)-poly(propylene oxide) block copolymers have been obtained[29], in conformity with Eqn.(4), by the condensation of α,ω-dihydroxypoly(ethylene oxide) with poly(propylene oxide) α,ω-bischloroformate. The chloroformate derivative of α,ω-dihydroxypoly(propylene oxide) was obtained with the aid of phosgene, which behaves in this instance as a functional group substituting agent:



(13)

(14)

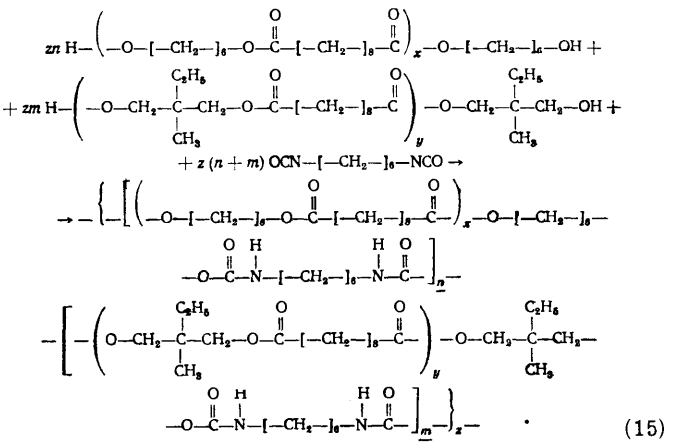
In the resulting block copolymers the crystalline lamellar phase consists of poly(ethylene oxide) blocks and the amorphous phase is made up of poly(propylene oxide) blocks. According to dilatometric data, the degree of

crystallinity of multiblock copolymers is lower by 60% than the degree of crystallinity of the corresponding three-block copolymers. The crystallinity of the specimens increased when the latter were annealed; the melting points of the block copolymers ranged from 37° to 56°C depending on composition [29].

Irregular (ol + m-Cl) multiblock poly(2,6-dimethylphenylene oxide)-poly(2,6-diphenylene oxide) block copolymers have been obtained by the dehydropolycondensation of 2,6-dimethylphenyl in the presence of oligo-(2,6-diphenylphenylene oxide) [30]. Oxidation of a mixture of 2,6-dimethylphenol with 2,6-diphenylphenol leads to the formation of a statistical copolymer; oxidation of 2,6-diphenylphenol in the presence of poly-(2,6-dimethylphenylene oxide) prepared beforehand leads to a mixture of part of the initial polymer and of the newly formed statistical copolymer as a result of exchange processes occurring in the course of dehydropolycondensation. Depending on the method of isolation of the block copolymer from the reaction mixture, the oligo-(2,6-dimethylphenylene oxide) blocks can constitute the amorphous or crystalline phase. The oligo-(2,6-dimethylphenylene oxide) blocks in the isolated copolymer always constitute the amorphous phase, but they crystallise on heating, while oligo(2,6-diphenyl oxide) blocks become amorphous. The block copolymers synthesised are inhomogeneous with respect to chemical composition: on heating their solutions in *m*-xylene, macromolecules enriched in oligo-(2,6-diphenylphenylene oxide) blocks are precipitated.

2. Polyester–Polyester Block Copolymers

There are numerous examples of the synthesis of two-component block copolymers the constituent block of which consists of polyesters. In particular, the reaction of a mixture of two hydroxylated or carboxylated low-molecular-weight aliphatic [poly(ethylene sebacate), poly-(ethylene succinate), poly(ethylene adipate) and poly-(propylene adipate) [31], poly(butylene saccinate) and poly(butylene sebacate) [32], poly(hexamethylene sebacate) and poly-(2-ethyl-2-methyl-1,3-propylene sebacate) [33] or aromatic and aliphatic [poly(ethylene terephthalate) and poly(ethylene succinate) poly(ethylene adipate), etc. [34]] polyesters with di-isocyanates yielded irregular (ol-1 + ol-2 + cl) block polymers:



(15)

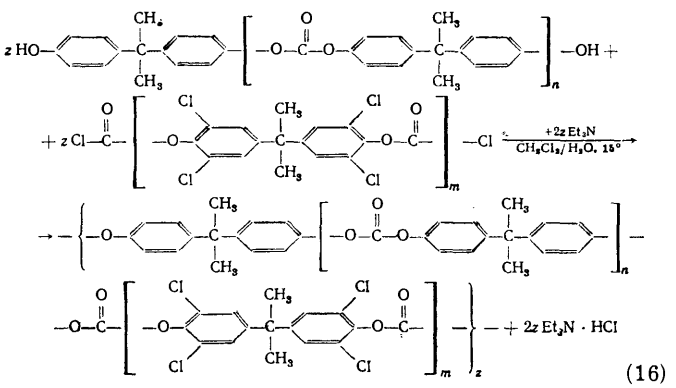
Multiblock poly(hexamethylene sebacate)–poly(2-ethyl-2-methyl-1,3-propylene sebacate) block copolymers [see Eqn.(15)] contain blocks consisting of isomeric polymers having identical chemical compositions but different chemical structures: the first polymer is highly crystalline with $T_m = -70°C$, while the second is entirely amorphous; its $T_g = -69°C$. [33] These block copolymers contain crystalline and amorphous phases and, as the content of crystallising oligo-(hexamethylene sebacate) blocks in the block copolymer increases, i.e. as the number of these blocks in the macrochain diminishes, the degree of crystallinity of the block copolymers increases. It has been suggested that [35] this is associated with the marked dependence of the crystallinity of the blocks on their molecular weight, i.e. on the fact that an isolated block as it were recovers its initial length, whereupon its ability to crystallise and undergo aggregation with other crystallising blocks of the same type becomes more marked. Dielectric relaxation studies on specimens have shown that β-relaxation processes in block copolymers depend on their composition and are associated with the relaxation of the polymethylene chain fragments [36].

Irregular (ol + cm + cm-cl) polyester–polyester block copolymers have been obtained from oligo(butylene adipate) with terminal hydroxy-groups, butylene glycol, and dimethyl terephthalate [37]. These block copolymers manifest the properties of thermoelastoplastic materials.

Regularly alternating poly(decamethylene terephthalate)–poly(decamethylene isophthalate) block copolymers have been obtained by the reaction of previously formed oligomers, one of which contained hydroxy-groups and the other contained acid chloride functional groups [38]. The same method has been used to synthesis other similar block copolymers.

3. Polycarbonate–Polycarbonate Block Copolymers

A typical method for the synthesis of these block copolymers involves the interaction of two reaction solutions containing oligocarbonates with hydroxy- or chloroformyl terminal functional groups synthesised by interfacial polycondensation from various bisphenols [29]



(16)

The thermalstabilities of polycarbonate–polycarbonate block copolymers are superior to those of statistical copolymers having an analogous composition. Some of them have been recommended as a base for photographic materials.

Polycarbonate–polycarbonate block copolymers can also be obtained by other synthetic procedures, for example, by the introduction of measured amounts of starting materials into the reaction medium, by the interaction of a mixture of an oligocarbonate prepared beforehand and a bisphenol with phosgene to give irregular (ol + cm + cm-cl) block copolymers, etc.

4. Polysulphide–Polysulphide Block Copolymers

Irregular (ol-1 + ol-2) aliphatic multiblock polysulphide–polysulphide block copolymers can be obtained by oxidising a mixture of two or more liquid (M.W. = 4000 to 8000) oligosulphides of various structure having terminal mercapto-groups[40]. Such block copolymers possess unique physicomechanical properties at low temperatures.

5. Polyamide–Polyamide Block Copolymers

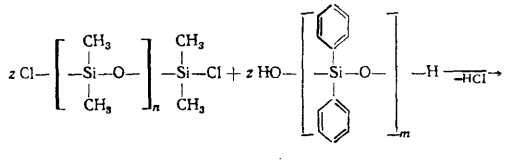
Polyamide–polyamide block copolymers of the polycondensation type can be obtained by a number of procedures, particularly by the polycondensation in the melt of a mixture of primary and secondary aliphatic–aromatic diamines, having appreciably different reactivities, with aliphatic dicarboxylic acids[41]. These crystallising irregular (cm-1 + cm-2 + cm-3) block copolymers consist of two phases and have two melting points.

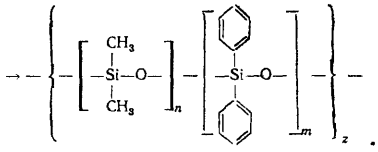
Irregular (ol-1 + ol-2 + cl) block copolymers have been obtained by the interaction of two diamino-oligoamides of different structure with di-isocyanates[42]. Two-component block copolymers with a regular alternation of polyamide blocks have been obtained by the interaction of diamino- and dichloroformyl-oligoamides synthesised from *trans*-2,5-dimethylpiperazine and the dichlorides of dicarboxylic acids such as terephthalic, isophthalic, and sebacic acids[43,44] and from *p*-diaminobiphenyl or *trans*-2,5-dimethylpiperazine and terephthalic or adipic acid dichloride[45,46].

6. Polyorganosiloxane–Polyorganosiloxane Block Copolymers

Block copolymers consisting of polyorganosiloxane blocks can be obtained in different ways; in particular, multiblock regularly alternating polydimethylsiloxane–polydiphenylsiloxane block copolymers of the polycondensation type have been obtained by the interaction of "living" block copolymers of the polymerisation type with a chain lengthening agent[47]. The initial four-block copolymer B–A–A–B was obtained by the polymerisation of hexamethylcyclotrisiloxane in the presence of an initiator (a complex of the dilithium salt of 1,1,3,3-tetraphenyldisiloxanediol with hexamethylphosphoramide) with subsequent addition and polymerisation of hexaphenylcyclotrisiloxane. When structured polydimethylsiloxane–polydiphenylsiloxane block copolymers are compared, the best properties are exhibited by multiblock copolymers. Both types of block copolymers have analogous morphologies, but the rate of formation of domains is higher for the multiblock copolymer. The continuous amorphous phase consists of polydimethylsiloxane and the dispersed phase consists of crystalline polydiphenylsiloxane domains[48].

Regularly alternating block copolymers can be obtained also by the heterofunctional condensation of oligosiloxanes, for example by the reaction of α,ω-dichloropolydimethylsiloxane with α,ω-dihydroxypolydiphenylsiloxane[49]:





(17)

They can also be synthesised by the reaction of polydiorganosiloxanediols with siloxane oligomers having terminal acetoxy-groups[50], alkoxy-groups, or hydrogen atoms.

Irregular (ol-1 + ol-2) polyorganosiloxane–polyorganosiloxane block copolymers can be obtained by the reaction (in the presence of catalysts) of two oligo-organosiloxanediols[49] or a mixture of two oligodiols and a silanol[51]. Readily structured irregular (ol + m-1-cl + m-2-cl) block copolymers can be obtained from oligo-organosiloxanediol, trichlorophenylsilane, and dichloromethylphenylsilane[52].

IV. TWO-TYPE BLOCK COPOLYMERS

Two-type block copolymers consist of polymer blocks belonging to two different types. Such block copolymers constitute the vast majority among block copolymers of the polycondensation type known hitherto. Two-type block copolymers may be synthesised for the following purposes: (a) for imparting elasticity to rigid-chain polymers; (b) for increasing the strength characteristics of elastomers; (c) for imparting hydrophilic properties to polymers; (d) for increasing the permeability of polymers to gases and the selectivity of their permeability; (e) for reducing the viscosity of melts of rigid-chain polymers; (f) for imparting antistatic properties to polymers; (g) for increasing the chemical stability of polymers; (h) for synthesising polymers capable of being degraded biologically, etc.

In order to achieve these aims, blocks of different polymers, having a wide variety of physicochemical properties, are combined in a single macromolecule. At the same time, whatever the properties of the constituent blocks of the block copolymers, they can be divided into (a) blocks with enhanced chain mobility (flexible blocks with a low thermal stability) and (b) blocks with a reduced chain mobility (rigid blocks with a high thermal stability). All two-type block copolymers can therefore be divided into the following groups:

A. Elastoplastic block copolymers (copolymers containing blocks with appreciably different thermal stabilities).

B. Thermoplastic block copolymers (copolymers containing blocks with relatively similar high thermal stabilities).

C. Elastomeric block copolymers (copolymers containing blocks with relatively similar low thermal stabilities).

A general list of block copolymers belonging to a particular group is presented in Table 2.

A. ELASTOPLASTIC BLOCK COPOLYMERS

1. Block Copolymers Containing Blocks Comprising Aliphatic Polyethers

Aliphatic polyethers are elastic crystallisable polymers. The presence of polar groups and the high flexibility of the macromolecules ensure a high solubility of the polymers in organic solvents. Poly(ethylene oxide) exhibits a

unique solubility in water. Some of the first block copolymers based on aliphatic polyethers were segmented polyurethanes incorporating polyurethane and polyurea block copolymers[1].

Table 2. Two-type block copolymers.

A. Elastoplastic block copolymers

Flexible block A	Rigid block B	References
Aliphatic polyether	Polyurethane*	14-17, 54-57
ditto	Polyurea*	14-17, 54-57
"	Polyester:	
"	aliphatic-aromatic	58-84
"	aromatic	84-87
"	Polycarbonate	88-92
"	Poly(arylene sulphone oxide)	93
"	Polyamide	94-100
"	Polystyrene	101-103
"	Cellulose	110-112
Aliphatic polyester	Polyurethane*	54-56
ditto	Polyurea*	54-56
"	Polycarbonate	88,113-115
"	Polyamide	116-117
Polydiene	Polyurethane*	55,56,61
"	Polyurea*	55,56,61
"	Polyamide	119
"	Polyimide	120
Aliphatic polysulphide	Polyurethane	121
ditto	Polyimidothioether	122
Polyorganosiloxane	Polyurethane*	54
ditto	Polyurea	54
"	Polytetramethylenesilphenylene-siloxane	123-125
"	Polystyrene	126-129
"	Poly-α-methylstyrene	130
"	Polycarbonate**	131-140
"	Poly(arylene sulphone oxide)**	141-144
"	Aromatic polyether	145
"	Polyester:	
"	aliphatic-aromatic	146,147
"	aromatic	148-154
"	Polyamide	98,155
"	Polyimide	156

B. Thermoplastic Block Copolymers

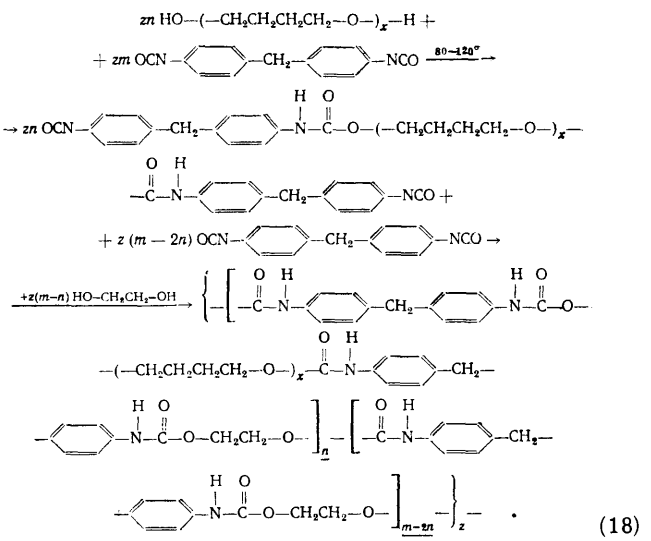
Rigid block A	Rigid block B	References
Polycarbonate	Polyurethane	157
ditto	Polystyrene	88,158
"	Poly(phenylene oxide)	159
"	Polyester (aliphatic-aromatic)	160
"	Poly(arylene sulphone oxide)	161,162
Poly(arylene sulphone oxide)	Polycarbonate	161,162
"	Polystyrene	8
"	Poly(phenylene oxide)	163
"	Polyester:	
"	aliphatic-aromatic	8
"	aromatic**	164,165
Polystyrene	Polycarbonate	88,158
ditto	Polyester	166
"	Poly(arylene sulphone oxide)	8
"	Polyamide	166
Polyether	Polycarbonate	159
ditto	Polyester	167
"	Poly(arylene sulphone oxide)	163
Polyester	Polycarbonate	160
ditto	Poly(arylene sulphone oxide)	8,164,165
"	Polystyrene	166
"	Polyether	167
"	Polyamide	168,169
Polyamide	Polystyrene	166
ditto	Polyester	168,169

C. Elastomeric Block Copolymers

Flexible block A	Flexible block B	References
Polydimethylsiloxane	Polyether*	7,170-172
ditto	Polyester	173

*Block copolymers manufactured on an industrial scale.
**Block copolymers manufactured in the form of experimental batches.

(a) Polyurethane–poly(alkylene oxide) block copolymers. Polyurethane–poly(alkylene oxide) block copolymers, which are some of the first block copolymers of the polycondensation type[53], consist of rigid polyurethane blocks (T_g† or T_m‡ in the range 100–250°C), obtained from a di-isocyanate and a low-molecular-weight glycol, and flexible poly(alkylene oxide) blocks ($T_g < 0$°C). Regularly alternating block copolymers are formed when equimolar amounts of oligo(urethane di-isocyanate) and oligo(alkene oxide)diol, obtained beforehand, are made to react. Irregular (ol + cm + cm-cl) copolymers are formed when all the starting materials are mixed simultaneously: the oligodiol, the low-molecular-weight glycol, and the di-isocyanate. However, irregular (ol + cm-fgs + cm-cl) urethane block copolymers, which are synthesised by a two-stage procedure, are nowadays of greatest importance, for example:



(18)

Oligoethers such as oligo(propylene oxide), oligo(tetramethylene oxide) etc. are used as the initial oligodiols with a molecular weight of 1000–3000 in the synthesis of polyurethane–poly(alkylene oxide) block copolymers; the initial di-isocyanates are methylenedi-(4-phenyl) di-isocyanate, tolylene di-isocyanate, 1,6-hexamethylene di-isocyanate, etc., and the initial low-molecular-weight glycols usually employed are 1,2-ethylene glycol, 1,4-tetramethylene glycol, etc.

Polyurethane–poly(alkylene oxide) block copolymers are microheterogeneous two-phase systems in which rigid oligourethane blocks, segregated into a separate phase owing to the incompatibility of the blocks, form 30–100 Å domains, greatly strengthened by strong intermolecular hydrogen bonds. Owing to the presence of a strong physical network, polyurethane block copolymers are very strong and hard and possess a high resistance to tearing and wear[14-17,54-57].

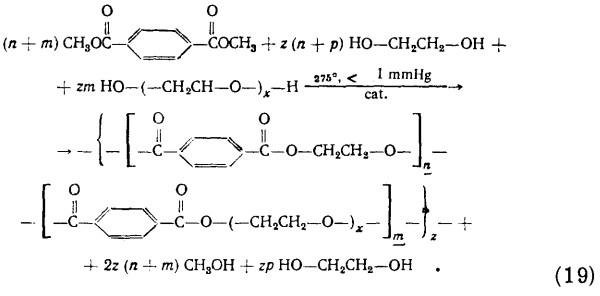
(b) Polyurea–poly(alkylene oxide) block copolymers. The principal difference between the synthesis of polyurethane–poly(alkylene oxide) and polyurea–poly(alkylene oxide) block copolymers involves the

† Glass point.

‡ Melting point.

use of diamines instead of glycols in the latter case. Owing to the presence of an excess of di-isocyanate [Eqn. (18)], the growth of rigid oligourea blocks is accompanied by the formation of a certain amount of biuret cross-links[55,56]. In contrast to polyurethane block copolymers, polyurea block copolymers are less stable in the melt but are harder. More detailed information about the synthesis and properties of polyurethane–poly(alkylene oxide) and polyurea–poly(alkylene oxide) block copolymers may be found in a number of reviews[14-17,54-57].

(c) Polyester–poly(alkylene oxide) block copolymers. Aliphaticaromatic or aromatic polyesters constitute the rigid blocks in block copolymers having this structure. Block copolymers containing rigid blocks of crystallising poly(ethylene terephthalate) (T_m = 265 °C) and flexible poly(ethylene oxide) blocks (T_m = 65 °C, T_g = −55 °C) as well as segmented polyurethanes were some of the first block copolymers of the polycondensation type synthesised[58-60]. Modification of poly(ethylene terephthalate) by replacing part of the ethylene glycol by oligo(ethylene oxide)diol with a molecular weight of 1000–6000 was undertaken in order to impart hydrophilic properties, an improved capacity for dyeing, and increased elasticity to poly(ethylene terephthalate) fibres. Irregular (ol + cm + cm-cl) poly(ethylene terephthalate)–poly(ethylene oxide) block copolymers, usually containing 20–30 wt.% of flexible blocks, are synthesised in the melt in the presence of a catalyst:

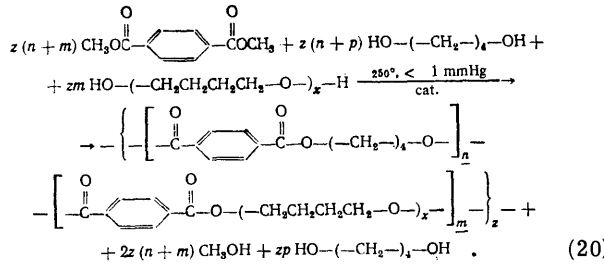


(19)

The disperse phase in the block copolymer is crystalline poly(ethylene terephthalate) and the continuous phase consists of amorphous poly(ethylene oxide) [oligo(ethylene oxide) blocks with a molecular weight of 1000–3000 remain amorphous, but, with increase of molecular weight to 6000, they may crystallise]. The poly(ethylene terephthalate) may be modified further by replacing part of the dimethyl terephthalate by dimethyl isophthalate[61] or by synthesising poly(ethylene terephthalate)–poly(tetramethylene oxide) block copolymers[62].

By analogy with poly(ethylene terephthalate)–poly(ethylene oxide) copolymers, it has been possible to synthesise in recent years poly(propylene terephthalate–poly(propylene oxide),[63] poly(tetramethylene terephthalate)–poly(propylene oxide),[64] poly(tetramethylene terephthalate)–poly(ethylene oxide),[65] poly(hexamethylene terephthalate)–poly(ethylene oxide),[66] and poly(alkylene terephthalate)–poly(tetramethylene oxide)[67] block copolymers. Among polymers of this type, the greatest interest attaches to poly(tetramethylene terephthalate)–poly(tetramethylene oxide) block copolymers, which are manufactured under the name Hytrel by the Du Pont Company.

Irregular (ol + cm + cm-ol) poly(tetramethylene terephthalate)–poly(tetramethylene oxide) block copolymers, initially intended for the synthesis of strong and elastic fibres[68], are synthesised in the melt in the presence of catalysts for equilibrium transesterification[69-71]:



(20)

The molecular weight of the initial oligo(tetramethylene oxide) (M.W. = 1000–4000) is usually 1000 and its content in the polymer is usually 30–70 wt.%.[70] In this composition range the block copolymer has in fact the most effective physicomechanical properties[70-82].

Owing to the presence of the crystalline phase, the block copolymers are insoluble in the majority of organic solvents. The rigid blocks in poly(tetramethylene terephthalate)–poly(tetramethylene oxide) copolymers crystallise very rapidly, so that there is no need for annealing articles made from this material, which cannot be said, for example, of poly(ethylene terephthalate)–poly(ethylene oxide) block copolymers, where the rate of crystallisation of rigid blocks is much lower[72]. The block copolymer containing 67% of the flexible blocks has T_m = 176 °C and T_g = −78 °C, the stress corresponding to 300% elongation is 110 kgf cm^{-2}, the tensile strength is 400 kgf cm^{-2}, and the relative elongation on rupture is 800%.

The block copolymers possess an unusual two-phase structure and consist of continuous (and not discrete) and interacting crystalline (in the form of lamellae) and amorphous domains[73].

Industrial brands of the Hytrel polymer contain a small amount of tetramethylene isophthalate units[70,82] and, depending on composition, have a tensile strength of 350 to 450 kgf cm^{-2} and a relative elongation on rupture of 500–600%. The block copolymers possess useful rheological properties and their melts have low viscosities and high stabilities and can be processed by rotational casting, casting under pressure, etc.[83] They are also distinguished by a high chemical stability, resistance to repeated deformation, and resistance to tearing, wear, and creep.

Irregular (ol + cm + cm-cl) block copolymers containing rigid aromatic polyester blocks (polyarylates) and flexible poly(ethylene oxide) or poly(propylene oxide) blocks have been obtained by high-temperature polycondensation in solution by the interaction of a mixture of a bisphenol, terephthalic acid dichloride, and oligo(alkylene oxide) diols[84,85]. The block copolymers exhibited high thermal stability and a solubility in organic solvents higher than that of polyarylates, but the increase in their elasticity was insignificant. At the same time regularly alternating, polyarylate–poly(ethylene oxide) block copolymers, obtained under the conditions of low-temperature polycondensation in solution from oligo(ethylene oxide) bischloroformate (M.W. = 1000–2000) and oligoarylate diol based on 2,2-di(4-hydroxyphenyl)propane and terephthalic acid dichloride, exhibit a high strength (100 to 350 kgf cm^{-2}) and a high relative elongation on rupture (700–400%) respectively. There are polyarylate and poly(alkylene oxide) crystalline and amorphous phases

respectively in these polymers and on extension the specimens are strengthened[86].

Regularly alternating polyarylate–poly(ethylene oxide) block copolymers containing blocks of amorphous polyarylate based on phenolphthalein and terephthalic acid dichloride (1000–5000) and poly(ethylene oxide) blocks (400–20 000) have been obtained under the conditions of acceptor-catalytic polycondensation from dihydroxyoligoarylates and dihydroxyoligo(ethylene oxides)[87]. Terephthalic acid dichloride and not phosgene[86] was used as the functional group substituting agent. When the molecular weights of the oligo(ethylene oxide) blocks are low, these block copolymers are amorphous, but, with increased molecular weight of the flexible blocks (2000 to 20 000), they become segregated in a separate phase and crystallise. The block copolymers exhibit a high strength (200–1000 kgf cm^{-2}) and a large relative elongation on rupture (800–100%).

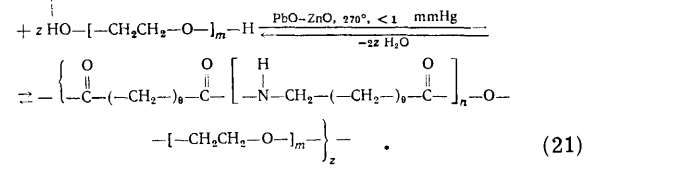
(d) Polycarbonate–poly(alkylene oxide) block copolymers. Regularly alternating block copolymers containing rigid oligocarbonate blocks based on 2,2-di-(4-hydroxyphenyl)propane and phosgene and flexible blocks of poly(ethylene oxide) or poly(tetramethylene oxide) are formed under the conditions of interfacial polycondensation from an oligocarbonate diol (2000 to 4700) obtained beforehand and an oligo(alkylene oxide) (1000–3000) with terminal chloroformate groups[88,89]. These block copolymers have fairly effective mechanical properties. Their strength is 100–150 kgf cm^{-2} and their relative elongation on rupture is >200%. The rate of crystallisation of oligocarbonate blocks in the copolymers is much higher than the rate of crystallisation of homopolycarbonate. There is a poly(alkylene oxide) amorphous phase in the block copolymers, but, when the molecular weight of the flexible blocks reaches 3000, a second crystalline phase is observed.

Irregular (ol + cm + cm-cl) polycarbonate–poly(alkylene oxide) block copolymers have been obtained by low-temperature polycondensation in solution from a mixture of oligo(alkylene oxide) diol [poly(ethylene oxide), poly(propylene oxide), and poly(tetramethylene oxide)], 2,2-di-(4-hydroxyphenyl)propane, and phosgene[90]. Block copolymers containing approximately 50 wt.% of oligo(ethylene oxide) blocks (4000–6000) have effective mechanical properties: an ultimate strength of 500 kgf cm^{-2} and a relative elongation on rupture of 600%. Block copolymers containing amorphous oligocarbonate blocks based on bisphenols with bulky bridge groups have been synthesised by the same method[91]. It is suggested[91] that the bulky norbornene rings in the rigid blocks constitute the nodes of a physical network which reduces the mobility of the macromolecules and imparts to the block copolymers the properties of thermoelastoplastic materials.

(e) Poly(arylene sulphone oxide)–poly(alkylene oxide) block copolymers. Regularly alternating poly(arylene sulphone oxide)–poly(ethylene oxide) block copolymers have been obtained[92] in accordance with Eqn.(21) from oligo(arylene sulphone oxide) diols (2400, 4600, and 9100) based on 2,2-di-(4-hydroxyphenyl)-propane and di-(4-chlorophenyl) sulphone and oligo(ethylene oxides) (400, 1000, 3000, and 15 000) with terminal acid chloride groups. Block copolymers with short flexible blocks (400–3000) consist of a single phase and have effective mechanical properties. For example, the copolymer containing 58 wt.% of rigid blocks with M.W. = 4600 and 42 wt.% of flexible blocks with M.W. = 3000 has an ultimate strength of 280 kgf cm^{-2} and a relative elongation on rupture of 460%. However, block copolymers with long (M.W. = 15 000) oligo(ethylene oxide) blocks have been found to contain a crystalline phase of the latter and such polymers have low values of the parameters characterising the mechanical properties; for example, the ultimate strength of a copolymer with rigid blocks having M.W. = 4600 and flexible blocks having M.W. = 15 000 is 180 kgf cm^{-2} and the relative elongation on rupture is 5%. Depending on composition, poly(arylene sulphone oxide)–poly(ethylene oxide) block copolymers swell in water by 1–120% and have effective antistatic properties.

Regularly alternating poly(arylene sulphone oxide)–poly(tetramethylene oxide) block copolymers obtained from oligo(arylene sulphone oxide) diols and oligo(tetramethylene oxides) with terminal chloroformate groups have been described[93].

(f) Polyamide–poly(alkylene oxide) block copolymers. Regularly alternating block copolymers with aliphatic polyamide blocks (usually polyamide 6 or polyamide 6,6) and poly(alkylene oxide) blocks are formed when oligo(alkylene oxides), in which the terminal hydroxy-groups have been substituted (in one or several stages) by isocyanate[94] or amino-groups[95], interact with oligoamines having terminal amino- or carboxy-groups. A dehydration reaction has been used recently to synthesise regularly alternating polyamide(11)–poly(ethylene oxide) block copolymers[96,97]:



(21)

The initial oligomers are incompatible, so that the reaction proceeds initially in a heterogeneous medium. The heterogeneity of the melt disappears if 10 wt.% of the finished block copolymer is added to the mixture of oligomers before the reaction[97]. The block copolymers can be used as thermoelastoplastic materials or as elastic fibres.

In order to reduce T_g and to improve the capacity of aromatic polyamides for being processed, multiblock irregular (ol + cm-fgs + cm-cl), irregular (ol + fgs + cm-fgs + cm-cl), and three-block polymetaphenyleneisophthalamide–poly(ethylene oxide) block copolymers have been synthesised[98]. They consist of two phases: the poly(ethylene oxide) phase (molecular weight of blocks 1000–6000) is dispersed in the continuous polyamide phase[99,100]. The rheological and physicomechanical properties of the copolymers have not been published as yet.

(g) Polystyrene–poly(alkylene oxide) block copolymers. Multiblock regularly alternating polystyrene–poly(ethylene oxide) block copolymers have been obtained by increasing the chain lengths of three-block poly(ethylene oxide)–polystyrene–poly(ethylene oxide) copolymers of the polymerisation type having terminal hydroxy-groups with phosgene or a dicarboxylic acid dichloride[101]. Another method of synthesis of the block copolymers consists in the interaction of an oligostyrene di-isocyanate (2000–6000) with an oligo(ethylene oxide)diol (400–6000).[102] The block copolymers exhibit

an enhanced capacity (compared with polystyrene) for absorbing atmospheric moisture, which increases with increasing content of hydrophilic blocks. Polystyrene–poly(ethylene oxide) copolymers are amorphous, but, during isothermal annealing, the segregation of oligo(ethylene oxide) blocks in a separate phase initiated by crystallisation is observed. The maximum rate of crystallisation has been noted for blocks with M.W. = 6000: they form twofold and threefold structures incorporated in crystalline domains [103]. The block copolymers containing flexible blocks with M.W. = 2000 do not crystallise. The short blocks in such copolymers act as plasticisers, lowering the temperature of the α-transitions of the polystyrene blocks [104].

Regularly alternating polystyrene–poly(ethylene oxide) block copolymers can also be obtained by converting a "living" oligostyrene with terminal carbanionic groups under the influence of an excess of phosgene into a bischloroformate with its subsequent polycondensation with an oligo(ethylene oxide) diol [105].

Two-block and three-block polystyrene–poly(tetramethylene oxide) block copolymers have been obtained by the reaction of a "living" oligo(tetramethylene oxide) cation or dication and a "living" oligostyrene anion [106]. Multiblock regularly alternating polystyrene–poly(tetramethylene oxide) block copolymers are formed in the interaction of an oligo(tetramethylene oxide) dication and an oligo-styrene dicarboxylate, used instead of the oligostyrene dianion, because the latter is involved in side reactions [107] [Eqn.(22)]. Block copolymers having an analogous structure have been obtained by the interaction of oligostyrene [108] or oligo-α-methylstyrene [109] dianions with an oligo(tetramethylene oxide) dication obtained with the aid of the $AgPF_6$–alkyl bromide initiator. It is suggested that the reaction between "living" polymeric dianions and dications is accompanied by the elimination of a tetrahydrofuran molecule.

(h) Cellulose–poly(alkylene oxide) block copolymers. Regularly alternating cellulose–poly(alkylene oxide) block copolymers have been obtained by the reaction of substituted, for example, acetylated, cellulose oligomers having terminal hydroxy-groups with oligo(alkylene oxides) having terminal isocyanate groups [110–112] [Eqn. (23)]. Acetylation of cellulose makes it possible to carry out its oligomerisation and at the same time increase its resistance to biodegradation. If the block copolymers synthesised are subjected to deacetylation, the result is the formation of cellulose–poly(propylene oxide) block copolymers capable of undergoing enzymatic hydrolysis. Biodegradation of the block copolymers takes place under these conditions many times faster than the degradation of cellulose [111,112].

The introduction of oligomeric cellulose blocks and other polymers capable of biodegradation (starch, casein, gelatin, etc.) into the macromolecules of the polymers used to prepare mass consumption articles is of considerable interest in view of the problem of the protection of the environment. It appears that the synthesis of block copolymers capable of biodegradation and having acceptable physicomechanical properties may become one of the approaches to the solution of this problem.

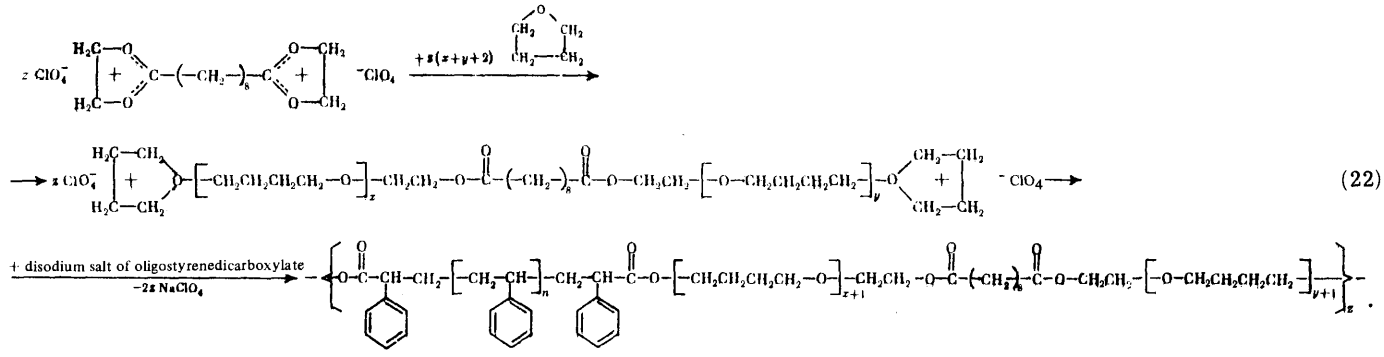
2. Block Copolymers Containing Aliphatic Polyester Blocks

Aliphatic polyesters are elastic crystallisable polymers with low melting and glass points. In this sense they are important for the synthesis of block copolymers of the polycondensation type, although their properties are inferior to those of polyethers.

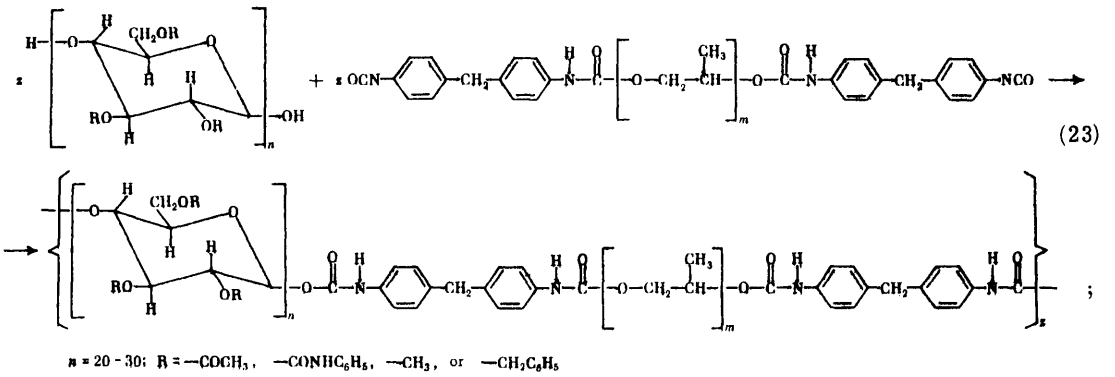
(a) Polyurethane–polyester block copolymers. These block copolymers consist of rigid polyurethane blocks, obtained from a di-isocyanate and a low-molecular weight glycol, and flexible polyester blocks with M.W. = 1000–3000. Oligo(ethylene adipate), oligo(ethylene sebacate), oligo(tetramethylene adipate), etc. are usually employed as the initial oligoesters with terminal hydroxy-groups. Among polyurethane–polyester block copolymers, irregular (ol + cm-fgs + cm-cl) copolymers [Eqn.(18)] have acquired the greatest practical importance. In contrast to the analogous polyurethane–polyether block copolymers, segmented polyurethanes based on aliphatic polyesters exhibit a much lower hydrolytic stability [54–56].

(b) Polyurea–polyester block copolymers. These block copolymers are synthesised in accordance with the same principle as polyurethane–polyester block copolymers. The difference is that, instead of a low-molecular-weight glycol [Eqn.(18)], a diamine is used [54–56].

(c) Polycarbonate–polyester block copolymers. Regularly alternating polycarbonate–poly(ethylene adipate) block copolymers have been obtained by the reaction of oligo(ethylene adipate) bischloroformate with oligocarbonatediol [88]. Irregular (ol + cm + cm-cl) block copolymers have been obtained by the reaction of a mixture of oligocarbonatediol based on 2,2-di-(4-hydroxyphenyl)propane and an oligocaprolactonediol with phosgene [113].



(22)



(23)

n = 20 - 30; R = —COCH$_3$, —CONHC$_6$H$_5$, —CH$_3$, or —CH$_2$C$_6$H$_5$

These block copolymers have the properties of thermoelastoplastic materials. Annealing of the specimens appreciably accelerates the crystallisation of the polycarbonate domains uniformly distributed in the amorphous polyester phase.

A series of other irregular polycarbonate–polycaprolactone block copolymers containing polycarbonate blocks based on 2,2,4,4-tetramethylcyclobutanediol [114] and various bisphenols [115] have also been described.

(d) Polyamide–polyester block copolymers. Regularly alternating polyamide(12)–poly(ethylene adipate) block copolymers have been obtained in the melt from aliphatic oligoamides with terminal carboxy-groups and oligo(ethylene adipates) with terminal hydroxy-groups [116]. The block copolymers exhibit a high strength and elasticity. The structure of the copolymers is appreciably influenced by exchange side processes.

Block copolymers consisting of rigid aromatic polyamide blocks and flexible polycaprolactone blocks have been obtained by the reaction of an oligocaprolactone having terminal isocyanate groups and an oligoamide having terminal amino-groups [117].

3. Block Copolymers Containing Diene Polymer Blocks

Polydienes (polybutadiene, polyisoprene, polypiperylene, polychloroprene, etc.) are elastic polymers capable of crystallisation only at very low temperatures. Owing to the high mobility of their macromolecules, polydienes have low glass points; for example $T_g = -108°C$ for *cis*-1,4-polybutadiene. The possibilities for the synthesis of block copolymers containing flexible polydiene blocks have greatly increased recently in connection with the development of the industrial manufacture of living "rubbers" [118].

(a) Polyurethane–polydiene and polyurea–polydiene block copolymers. Among segmented polyurethanes, block copolymers consisting of rigid oligourethane or oligourea blocks and flexible oligodiene blocks (polybutadiene, polyisoprene, copolymers of butadiene with acrylonitrile and isoprene, etc.) have been acquiring increasing importance recently. These block copolymers have the properties of thermoelastoplastic materials and exhibit a high hydrolytic stability [55,56,61].

(b) Polyamide–polydiene block copolymers. Irregular (ol-1 + ol-2 + cl) poly-ϵ-caprolactam–polybutadiene block copolymers have been synthesised [119]; oligo-ϵ-caprolactam with terminal amino-groups, oligobutadienediol, and 4,4′-diphenylmethane di-isocyanate were used as the initial compounds.

(c) Polyimide–polydiene block copolymers. Irregular (ol + cm + cm-cl) multiblock polyimide–polybutadiene block copolymers have been obtained from an oligobutadiene having terminal amino-groups, *m*-phenylenediamine, and the dianhydride of benzophenonetetracarboxylic acid [120].

4. Block Copolymers Containing Aliphatic Polysulphides

Aliphatic polysulphides (thiokols) are elastic polymers capable of crystallising on extension; the glass points of polysulphide rubbers are in the range from −20° to −60°C. Both polydisulphides and polytetrasulphides are special purpose rubbers characterised by high resistance to swelling in solvents, fuels, and oils, resistance to ozone and sunlight, and reduced permeability to moisture and gases.

(a) Polyurethane–polysulphide block copolymers. Block copolymers consisting of rigid oligourethane and flexible aliphatic oligosulphide blocks are obtained using oligosulphidedithiols, di-isocyanates, and glycols as the initial compounds. Polyurethane–polysulphide block copolymers have lower values of T_g compared with polyurethane–polyester block copolymers and exhibit a satisfactory radiation stability [121].

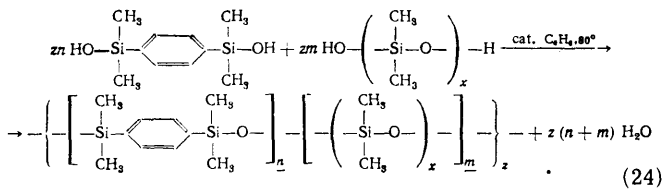
(b) Polyimidothioether–polysulphide block copolymers. Irregular (ol + cm-fgs + cm-cl) polyimidothioether–polysulphide block copolymers have been obtained from an oligosulphidedithiol, bismaleimide, and hydrogen sulphide [122]. These block copolymers exhibit the properties of thermoelastoplastic materials and are insoluble in organic solvents. A great obstacle to the processing of block copolymers via the melt is the low thermal stability of the polysulphide blocks, whose degradation begins at 200°C.

5. Block Copolymers Containing Polyorganosiloxane Blocks

(a) Polyurethane–polyorganosiloxane and polyurea–polyorganosiloxane block copolymers. Segmented polyurethanes containing flexible polyorganosiloxane blocks exhibit an enhanced thermal stability compared with polyurethanes based on oligoethers,

have effective low-temperature properties, and exhibit a high resistance to tearing[54].

(b) Polytetramethylsilphenylenesiloxane–polydimethylsiloxane block copolymers. Irregular (ol + m-cm) polytetramethyl-*para*-silphenylenesiloxane–polydimethylsiloxane block copolymers have been obtained in the presence of non-equilibrating catalysts from oligodimethylsiloxanediol and tetramethyl-*para*-silphenylenesiloxane[123]:



(24)

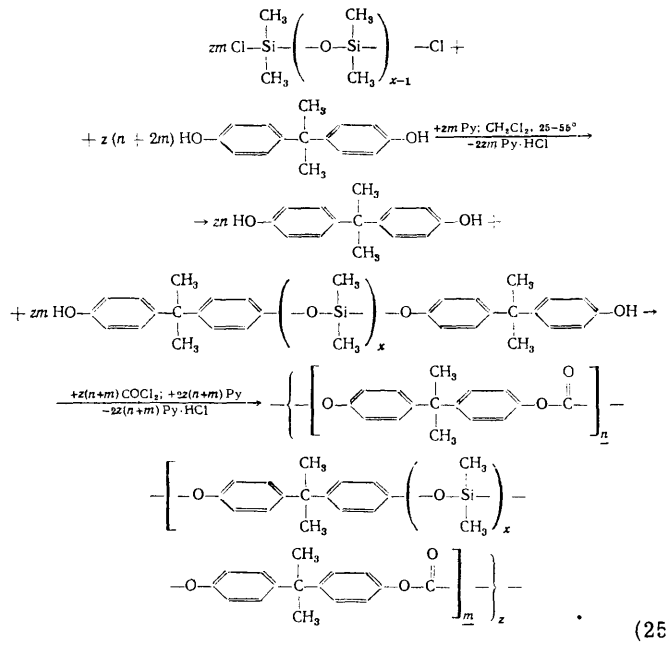
The block copolymers obtained comprise two phases: the continuous phase consists of amorphous polydimethylsiloxane blocks and the disperse phase is made up of crystalline domains of polytetramethyl-*para*-silphenylenesiloxane blocks which melt in the temperature range from 25° to 139°C, depending on the composition of the copolymers[124]. The block copolymers manifest the properties of thermoelastoplastic materials, have a strength of 70 to 200 kgf cm^{-2}, and a relative elongation on rupture of 500–960%.[125]

(c) Polystyrene–polydimethylsiloxane block copolymers. Regularly alternating polystyrene–polydimethylsiloxane block copolymers of the type $-(A-B-A-)_n$ have been obtained by the interaction of "living" polydimethylsiloxane–polystyrene–polydimethylsiloxane block copolymers of the polymerisation type with chain elongating agents such as diacetoxydiphenylsilane, dialkyldichlorosilanes, or dichloromethyltrifluoropropylsilane[126,127]. These block copolymers constitute a two-phase system comprising a continuous polydimethylsiloxane phase with $T_g = -120$°C and a disperse polystyrene phase with $T_g = 50$°C. The polymers have the properties of thermoelastoplastic materials, possess effective dielectric properties, and exhibit a high permeability to gases[128].

Regularly alternating block copolymers of the type $-(-A-B-)_n-$ have been obtained by the dehydropolycondensation of polydimethylsiloxane–polystyrene–polydimethylsiloxane A–B–A block copolymers having terminal hydroxy-groups in the presence of a catalyst[129].

(d) Poly-α-methylstyrene–polydimethylsiloxane block copolymers. Regularly alternating poly-α-methylstyrene–polydimethylsiloxane block copolymers of the type $-(-A-B-)_n-$ have been obtained by the polycondensation of oligo-α-methylstyrenediols and oligodimethylsiloxanes having terminal dimethylamino-groups in chlorinated aromatic solvents at 120° to 180°C.[130] The low reactivity of the hydroxy-groups in the aliphatic terminal units of oligo-α-methylstyrenediols may be increased with the aid of carbon dioxide, which catalyses the reaction. The block copolymers consist of two phases and have the properties of thermoelastoplastic materials. The replacement of polystyrene blocks by poly-α-methylstyrene blocks ($T_g = 170$°C) made it possible to extent the temperature range where the block copolymers are useful from between −100°C and +50°C to between −100°C and +130°C.

(e) Polycarbonate–polydimethylsiloxane block copolymers. Irregular (ol + cm-fgs + cm) polycarbonate–polydimethylsiloxane block copolymers have been obtained by treating with phosgene a mixture of 2,2-di-(4-hydroxyphenyl)propane and an oligodimethylsiloxane having terminal phenolic groups[131–133]:



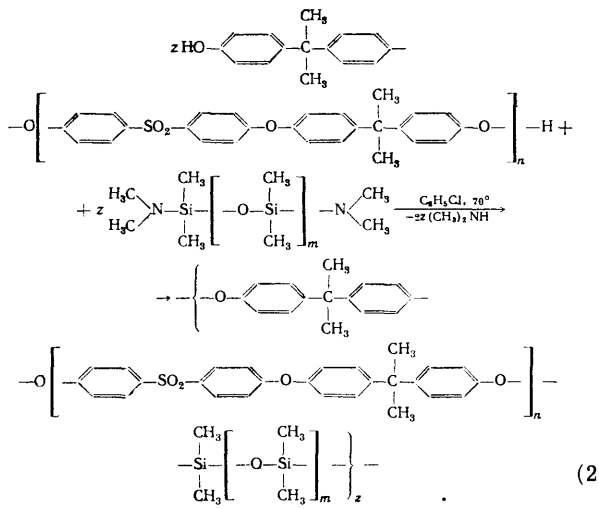
(25)

The block copolymers consist of two phases and manifest the properties of thermoelastoplastic materials. With increase in the content of rigid oligocarbonate blocks from 35 to 85%, the ultimate strength rises from 70 to 420 kgf cm^{-2} and the relative elongation on rupture falls from 800 to 100%.[133] The glass point of the continuous polydimethylsiloxane phase depends little on the length of the flexible blocks and is in the region of −110°C; on the other hand, T_g for the polycarbonate domains depends markedly on the length of the rigid blocks, varying from 60°C for blocks with five elementary units in the chain to 140°C for blocks with 46 repeating units. Crystallisation of the polycarbonate domains is observed when the block copolymer films are kept in ethyl methyl ketone or its vapour[134]. The solvent greatly influences the morphology of the block copolymer films obtained by casting from solutions[133]. The thermal stability of the block copolymers is somewhat inferior to that of homopolycarbonate[135]. Polycarbonate–polydimethylsiloxanes have useful dielectric properties[136] and a high permeability to gases[137]. Membranes based on them are used in apparatus designed for the enrichment of air in oxygen and for the oxygenation of blood. The block copolymers can be employed as coatings and adhesives[131].

Regularly alternating[138] and irregular (ol + cm-fgs + cm) polycarbonate–polydimethylsiloxane block copolymers based on cardobisphenols[139] and 2,2,4,4-tetramethylcyclobutane-1,3-diol[140] have also been obtained.

(f) Poly(arylene sulphone oxide)–polydimethylsiloxane block copolymers. Regularly alternating poly(arylene sulphone oxide)–polydimethylsiloxane block copolymers have been obtained by the interaction of equimolar amounts of an oligo(arylene

sulphone oxide)diol and an oligodimethylsiloxane having terminal dimethylamino-groups [141,142]:



(26)

Such block copolymers consist of two phases and exhibit the properties of thermoelastoplastic materials. The glass point of the polydimethylsiloxane phase is −120°C and that of the poly(arylene sulphone oxide) phase is +160°C, the ultimate strength of block copolymers containing 50–70 wt.% of the organosilicon phase is 100–180 kgf cm^{-2} and the relative elongation is 500–350%.[142] The block copolymers are resistant to hydrolysis, have a high thermal stability[142] and useful dielectric properties, and exhibit a high permeability to gases[143]. Poly(arylene sulphone oxide)–polydimethylsiloxane block copolymers can be used as film materials, as thermoelastoplastic substances with a wide range of working temperatures (from −120° to +160°C),[142] and as additives to poly(arylene sulphone oxides) (which increase their impact strength)[144].

(g) Poly(phenylene oxide)–polydimethylsiloxane block copolymers. Three-block poly(phenylene oxide)–polydimethylsiloxane block copolymers of the type A–B–A have been obtained by the reaction of an oligo(phenylene oxide) having a terminal hydroxy-group and an oligodimethylsiloxane having terminal isopropylamino-groups[145]. The block copolymers may be used as electrically insulating and thermally shrinkable films.

(h) Polyester–polydimethylsiloxane block copolymers. Regularly alternating poly(hexamethylene sebacate)–polydimethylsiloxane block copolymers have been obtained by the reaction of oligo(hexamethylene sebacate)diols and oligodimethylsiloxanes having terminal dimethylamino-[146] or chloro-groups[147]. The block copolymers consist of two phases. The rigid phase with T_m = 57°C is highly crystalline and consists of spherulites.

Regularly alternating block copolymers containing rigid blocks based on 2,2-di-(4-hydroxyphenyl)propane and isophthalic or terephthalic acid dichloride consist of two phases and exhibit the properties of thermoelastoplastic materials. The glass points of the flexible and rigid phases are −125°C and between +120°C and +135°C respectively and the melting point of the rigid phase is 295 and 260°C for the copolymers obtained from the dichlorides of terephthalic and isophthalic acids respectively[148].

Regularly alternating block copolymers containing amorphous blocks based on bisphenols and phthalic acid dichlorides have also been synthesised. Polyarylate–polydimethylsiloxane block copolymers are made up of two phases and exhibit the properties of thermoelastoplastic materials[149–151]. A high degree of segregation of the rigid and flexible blocks is observed in the block copolymers; the domains of the polyarylate phase have a diameter of approximately 160 Å. Polyarylate–polydimethylsiloxanes have high hydrolytic[152] and thermal[153] stabilities, effective electrically insulating properties, and a high permeability to gases. The properties of the resulting films are greatly influenced by the solvent[154].

(i) Polyamide–polydimethylsiloxane and polyimide–polydimethylsiloxane block copolymers. Regularly alternating polyamide–polydimethylsiloxane block copolymers have been obtained by the reaction of oligoamidediols based on α-amino-acids and oligodimethylsiloxanes having terminal dimethylamino-groups[155] and by the reaction of oligo-*meta*-phenyleneisophthalamides having terminal amino-groups and oligodimethylsiloxanes having terminal acid chloride groups[98]. The synthesis of regular (ol + fgs + cm-fgs + cm-cl) poly-*meta*-phenyleneisophthalamide–polydimethylsiloxane block copolymers has been described[98].

Regularly alternating polyimide–polydimethylsiloxane block copolymers have been synthesised by the reaction of oligoimides having terminal anhydride groups and oligodimethylsiloxanes having terminal aminoalkyl groups[156].

B. THERMOPLASTIC BLOCK COPOLYMERS

Thermoplastic block copolymers consist of thermoplastic polymer blocks.

1. Block Copolymers Containing Polycarbonate Blocks

(a) Polycarbonate–polyurethane block copolymers. Irregular (ol + cm + cm-cl) polycarbonate–polyurethane block copolymers have been obtained by the reaction with phosgene of a mixture of an aromatic oligourethanediol and 2,2-di-(4,4-hydroxyphenyl)propane or by the reaction of a mixture of an aromatic oligourethane bischloroformate and phosgene with 2,2-di-(4-hydroxyphenyl)propane[157].

Articles made from modified polycarbonates (for example, the base used for photographic film and recording tape) exhibit a high stability as regards size but, owing to the presence of aromatic polyurethane blocks, their thermal stability is reduced.

(b) Polycarbonate–polystyrene block copolymers. Regularly alternating polycarbonate–polystyrene block copolymers have been obtained by the interaction of oligostyrene bischloroformates with oligocarbonatediols[88].

Irregular (ol + cm + cm-cl) block copolymers have been synthesised by the reaction of a mixture of an oligostyrenediol [obtained by treating a "living" oligostyrene with phosgene and then with an excess of 2,2-di-(4-hydroxyphenyl)propane] and 2,2-di-(4-hydroxyphenyl)propane with phosgene[158]. Oligostyrenediols having molecular weights of 2900, 4100, and 9300 have been used to synthesise block copolymers. It was found that at 250°C the melts of the block copolymers have lower viscosities than that of the homopolycarbonate. The decrease of the viscosity

of the melt depends to a greater extent on the content of oligostyrene blocks (19, 22, and 29 wt.%) in the block copolymer than on their molecular weight.

(c) Polycarbonate–poly(phenylene oxide) block copolymers. Three-block polycarbonate–poly-(2,6-dimethylphenylene oxide) block copolymers of the type A–B–A having effective physicomechanical properties have been obtained by the reaction of an oligo-(phenylene oxide) having a terminal hydroxy-group with an oligocarbonate bischloroformate [159].

(d) Polycarbonate–polyester block copolymers. Irregular (ol + cm + cm-cl) polycarbonate–poly(ethylene terephthalate) block copolymers with satisfactory physicomechanical properties have been obtained in the melt from a mixture of oligo(ethylene terephthalate)diol, 2,2-di-(4-hydroxy-phenyl)propane, and diphenyl carbonate [160].

2. Block Copolymers Containing Poly(arylene sulphone oxide) Blocks

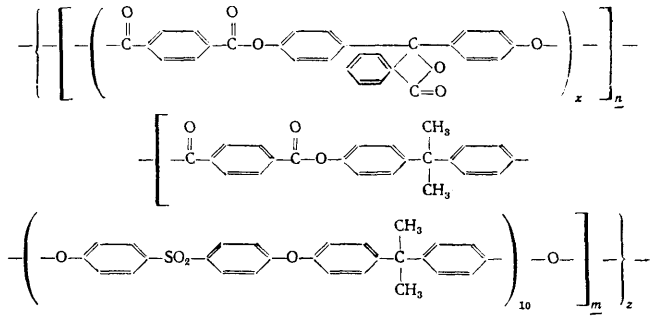
(a) Poly(arylene sulphone oxide)–polycarbonate block copolymers. Irregular (ol + cm + cm-cl), irregular (ol-1 + ol-2 + cl), and regularly alternating poly(arylene sulphone oxide)–polycarbonate block copolymers have been synthesised in three different ways [161]. The initial compounds were oligo(arylene sulphone oxide)diols based on 2,2-di-(4-hydroxyphenyl)-propane and di-(4-chlorophenyl) sulphone with molecular weights from 5000 to 26 000, oligocarbonatediols or oligo-carbonate bischloroformates based on 2,2-di-(4-hydroxy-phenyl)propane and phosgene with molecular weights from 5000 to 22 000, di-(4-hydroxyphenyl)propane, and phosgene. The resulting block copolymers of all three types and any composition were single-phase, despite the fact that the mixtures of the corresponding homopolymers and also the mixtures of the oligomers were heterophase. It has been suggested [162] that the formation of a second phase in the system can begin when oligomers with molecular weights greater than 22 000–26 000 are used. The glass points of the single-phase block copolymers depend on their composition and vary from 175° to 184°C. Furthermore, T_g depends also on the method of synthesis of the block copolymer; in particular, among irregular (ol + cm + cm-cl) and irregular (ol-1 + ol-2 + cl) block copolymers of the same composition, the irregular (ol-1 + ol-2 + cl) copolymer has a higher T_g. [161] Exposure of the specimens to acetone leads to the selective crystallisation of the oligocarbonate blocks, whereupon a single value of T_g and a single melting point T_m of the crystallites (T_m = 235°C) are observed.

(b) Poly(arylene sulphone oxide)–polystyrene block copolymers. Irregular (ol-1 + ol-2 + cl) poly(arylene sulphone oxide)–polystyrene block copolymers have been synthesised by the reaction of a mixture of oligo(arylene sulphone oxide)diol based on 2,2-di-(4-hydroxyphenyl)propane and di-(4-chlorophenyl)-sulphone and an oligostyrenediol with phosgene (Noshay and McGrath [8], p. 312). The block copolymers synthesised from oligomers with a molecular weight less than 4000 are single-phase, but if the molecular weight of the oligomer is greater than 4000, the block copolymers consist of two phases.

(c) Poly(arylene sulphone oxide)–poly-(phenylene oxide) block copolymers. Three-block poly(arylene sulphone oxide)–poly(phenylene oxide) block copolymers of the type A–B–A, suitable for the manufacture of cast articles and films, have been synthesised from oligo(phenylene oxides) having a terminal hydroxy-group and oligo(arylene sulphone oxides) having terminal acid chloride, chloroformate, or isocyanate groups [163].

(d) Poly(arylene sulphone oxide)–polyester block copolymers. Irregular (ol + cm + cm-cl) poly(arylene sulphone oxide)–poly(butylene terephthalate) block copolymers have been obtained by the reaction in boiling trichlorobenzene of an oligo(arylene sulphone oxide), having terminal acid chloride groups, and terephthalic acid dichloride with butylene glycol (Noshay and McGrath [8], p. 324). The glass point of the mixed amorphous phase in the block copolymers is 139°C and the melting point of the crystalline polyester phase is 200°C.

Poly(arylene sulphone oxides)–polyarylate block copolymers have been obtained in three different ways: (a) from pre-synthesised heterofunctional oligo(arylene sulphone oxides) and oligoarylates; (b) from homofunctional oligomers and the corresponding chain lengthening agents; (c) by introducing oligo(arylene sulphone oxides) into a mixture of initial low-molecular-weight compounds [164]:



where x is 10 for regularly alternating block copolymers, a multiple of 10 for irregular (ol-1 + ol-2 + cl) block copolymers, and ≥1 for irregular (ol + cm + cm-cl) block copolymers. Poly(arylene sulphone oxide)–polyarylate block copolymers consist of a single phase, while mixtures of the corresponding homopolymers and oligomers are heterophase. For low contents of oligo(arylene sulphone oxide) blocks in irregular (ol + cm + cm-cl) block copolymers, Young's modulus of elasticity, the ultimate tensile strength, and the relative elongation increase. This effect is very similar to the "antiplasticisation" effect observed for rigid-chain polymers plasticised by low-molecular-weight plasticisers.

It is especially interesting that the viscosity of melts of poly(arylene sulphone oxide)–polyarylate block copolymers varies non-additively with respect to the change in composition. A characteristic feature is a minimum in the viscosity of the melt for a relatively low content of oligo-(arylene sulphone oxide) blocks in the copolymers. The rheological characteristics of block copolymers of this composition are close to those of poly(arylene sulphone oxide) [165].

3. Block Copolymers Containing Polystyrene Blocks

Polystyrene–polycarbonate and polystyrene–poly(arylene sulphone oxide) block copolymers were described above.

(a) Polystyrene–polyester block copolymers. Irregular (ol + cm + cm-cl) polystyrene–poly(ethylene terephthalate) block copolymers have been obtained at 280°C in the presence of a catalyst from a mixture of an oligostyrenediol, ethylene glycol, and dimethyl terephthalate. The block copolymers consist of two phases; with increased content of crystallising polyester blocks in the copolymers, a uniform increase of the melting point and density of the block copolymers is observed [166].

(b) Polystyrene–polyamide block copolymers. Irregular (ol + m-cl) polystyrene–polyamide 6 and polystyrene–polyamide 6,6 block copolymers have been obtained by the interaction in the melt of a diammonium adipate salt derivative of oligostyrene (obtained by the interaction of oligostyrenediamine with adipic acid) with ϵ-aminocaproic acid or hexamethylene adipate (HA salt) respectively [166]. The block copolymers consist of an amorphous polystyrene phase and a crystalline polyamide phase. With increase of the content of crystallising blocks in the copolymers, a uniform increase of the melting point and density of the block copolymers is observed.

4. Block Copolymers Containing Polyether Blocks

Poly(phenylene oxide)–polycarbonate and poly(phenylene oxide)–poly(arylene sulphone oxide) block copolymers were described above.

Apart from these block copolymers, copolymers consisting of blocks of sulphonated polyethers, for example, those based on 2,2-di-(4-hydroxyphenyl)propane and 1,4-dichlorobutane, and polyester blocks, for example blocks based on ethylene glycol and dimethyl terephthalate, are known [167]. Irregular (ol + cm + cm-cl) polyether–polyester block copolymers have been obtained by the interaction of a mixture of a sulphonated polyetherdiol and glycol with dimethyl terephthalate. These block copolymers may be used as additives which increase the affinity of polyether [polyester?] fibres for basic dyes.

5. Block Copolymers Containing Polyester Blocks

Polyester–polycarbonate, polyester–poly(arylene sulphone oxide), polyester–polystyrene, and polyester–polyether block copolymers were described above.

Regularly alternating copolymers consisting of poly(ethylene terephthalate) and polyamide 6 [168] or polyamide 6,10 [169] blocks are also known. The block copolymers are obtained by the interaction of oligoamidedicarboxylic acids with oligoesterdiols [168] or by the reaction of oligoamidediamines with oligoesterdiacylchlorides [169].

C. ELASTOMERIC BLOCK COPOLYMERS

Elastomeric block copolymers consist of flexible rubberlike polymer blocks. A limited number of such block copolymers are known at the present time.

1. Polydimethylsiloxane–Poly(alkylene oxide) Block Copolymers

Linear polydimethylsiloxane–poly(alkylene oxide) block copolymers are formed when oligo(alkylene oxide)-diols interact with oligodimethylsiloxanes having acetoxy-, [170] dialkylamino-, [171] or isocyanate [172] end groups. These block copolymers are widely used as stabilisers ("silicone" surfactants) of polyurethane foams and also for the treatment of textile fibres (Allport and Janes [7], p. 342).

2. Polydimethylsiloxane–Polyester Block Copolymers

Irregular (ol + cm + cm-cl) polydimethylsiloxane–poly(butylene sebacate) block copolymers have been obtained from an oligodimethylsiloxane having terminal chloro-groups, butylene glycol, and sebacic acid dichloride; they may be used as loosening and levelling agents in electrophotographic compositions [173].

V. THREE- AND MULTI-TYPE BLOCK COPOLYMERS

Three-type block copolymers consist of polymer blocks of three different types [polyethers (polyesters?), polyorganosiloxanes, polydienes, polycarbonates, polyamides, etc.].

Very limited information is available at present about block copolymers of this kind; for example, the synthesis of five-block three-type polystyrene (A)–polybutadiene (B)–polyurea (C) block copolymers of the type A–B–C–B–A has been described [174], but no syntheses of multitype block copolymers have been published. In the future the synthesis of three- and multi-type block copolymers of the polycondensation type will undoubtedly be important in the manufacture of polymeric materials with a specified set of properties.

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Ladder Polyheteroarylenes—Progress and Problems

A.L.Rusanov

Survey of the present state of the chemistry of these polymers and examination of their resistance to various types of degradation show that a ladder structure does not guarantee great stability, although a high degree of structural perfection and highly stable heterocycles confer significantly improved heat resistance, thermal stability, non-flammability, radiation resistance, etc. relative to traditional heteroarylenes. The principal methods for synthesising ladder polyheteroarylenes of high degrees of cyclisation are considered, various modes of practical application are examined, and their prospects are noted. A list of 260 references is included.

CONTENTS

I. Introduction 62
II. Resistance to various types of degradation—preconditions and reality 62
III. Principal methods of synthesis 65
IV. Practical application—achievements and prospects 72
V. Conclusion 73

I. INTRODUCTION

The development of several modern technologies—primarily aviation, rocket manufacture, electrical engineering, electronics, etc.—made it necessary to produce polymeric materials with operating temperatures around 300°C. Solution of this problem largely involved the elaboration of novel thermostable polymers. For this reason many investigations were undertaken in the USSR and abroad from the mid-1950s with the aim of creating new thermostable macromolecular compounds[1]. These investigations led to a considerable number of heterorganic[1-9] and aromatic carbon-chain polymers[1,3,4,6-19] possessing a combination of valuable properties, but the greatest development occurred in the chemistry of aromatic polymers containing different heterocycles in the main chains—so called polyheteroarylenes[1,3,4,6-16,20-40].

The most widely used polyheteroarylenes have been polyimides[1,4,6-10,20,22,41,42] and polyazoles[1,4,6-10,21-32,40,43-47], whose development and introduction into industry solved the problem of producing polymeric materials capable of prolonged operation at temperatures up to 300°C. However, these polyheteroarylenes and materials made from them do not meet the constantly increasing demands, in particular for operation at temperatures above 300°C. During the mid-1960s, therefore, the development was undertaken of polyheteroarylenes that would surpass known heterocyclic polymers in a combination of properties, primarily in heat resistance and thermal stability. This problem could in principle be solved in several ways.

(1) Replacement of heterocyclic fragments in macromolecules of polyheteroarylenes by more thermostable heterocycles—an approach suggested by the preferential degradation of polyheteroarylenes at the heterocyclic fragments[48-56]—required a detailed study of the comparative thermal stability of individual heterocyclic systems[57-59] and the development of methods for synthesising polyheteroarylenes containing heterocycles of maximum thermal stability. This approach has now been followed quite successfully, although by no means all syntheses of highly thermostable aromatic heterocycles can be readily and successfully extended to polyheteroarylenes of high molecular weight.

(2) Polyheteroarylenes can be synthesised containing hetero-organic groups—e.g. organoboron[60,61] and organosilicon[62,63] groups.

(3) The production of polyheteroarylenes having a completely or partly ladder structure is the most promising approach, although quite controversial from various points of view. Ladder polymers—also termed "strip"[1], "double-chain", "ordered linear-spatial", and "non-randomly cross-linked"[64] polymers—attracted the close attention of investigators after the publication by Tessler[65,66] of results indicating that such polymers should be considerably more resistant to various types of degradation than are ordinary, "single-chain" polymers. The "period of enthusiasm" following his publications (1966-1970) saw the preparation of a considerable number of different classes of polyheteroarylenes, having a complete or partial ladder structure as a consequence of the introduction into the main chains of highly fused aromatic heterocycles[67-77]. Since in several cases such polymers differed little in thermal stability from the traditional polyheteroarylenes, interest in the ladder polymers diminished appreciably, and the "enthusiasm" was followed by a "period of scepticism", although research has continued on individual classes of ladder polymers.

Current views on ladder polyheteroarylenes can be summarised in the following statements: (i) partial and complete ladder structures can be expected to be more resistant than traditional polyheteroarylenes to various types of degradation; (ii) at the present time this potential advantage has not been realised; and (iii) the comparatively poor stability of known ladder polyheteroarylenes is due to the low degrees of cyclisation characterising all ladder polyheteroarylenes. All these statements are true within certain limits, but absolute acceptance of any of them will lead to erroneous conclusions, in particular to an unduly pessimistic assessment of ladder polyheteroarylenes.

An attempt has now been made at an objective survey of the present state of the chemistry of these polymers and their prospects.

II. RESISTANCE TO VARIOUS TYPES OF DEGRADATION—PRECONDITIONS AND REALITY

According to Tessler[65,66] great stability towards degradation of polymers having a complete or partial

ladder structure, in comparison with single-chain macromolecules, is a consequence of the following considerations. Any reaction involving rupture of the macromolecular chains of single-chain polymers will lead to a decrease in molecular mass of the latter and hence a decrease in their strength characteristics. Double-chain (ladder) polymers can undergo rupture of any one bond without decrease in molecular mass and impairment of strength properties. Moreover, random rupture of several bonds may also be unaccompanied by decrease in molecular mass, and only two "concerted" chain breakages, occurring at strictly defined sites, will lead to fracture of the macromolecule into two fragments with all its consequences.

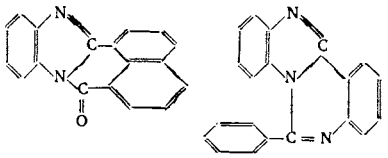
The above arguments were supported by quantitative results obtained by using the Monte Carlo method to analyse randomly occurring degradation processes in ladder and single-chain polymers [65,66]. The calculation was based on several postulates: (i) all bonds in the polymer were equally strong and equally accessible independently of their positions in macromolecules of different chain lengths; (ii) all polymer chains had the same length; and (iii) rates of degradation were proportional to the number of unbroken bonds in the polymer.

The calculations indicate that, for a given number of bonds ruptured in the macromolecules, completely laddered polymers undergo considerably smaller decreases in molecular mass than do single-chain polymers: in particular, the molecular mass of the former remains almost constant when the number of bonds broken would lead to an 80% decrease in single-chain polymers. Partly laddered structures occupy an intermediate position. In developing these principles Tessler [66] calculated rates of loss in weight of polymers of ladder and single-chain structure with increase in the number of bonds destroyed, and showed that in the initial stages of degradation ladder polymers undergo considerably smaller weight losses than do single-chain macromolecules.

Tessler's scheme is undoubtedly extremely empirical, since it disregards several factors—tending either to hinder or to promote degradation—among which the following may be mentioned. (i) Positive changes in entropy accompanying degradation are larger with ladder than with single-chain polymers, which facilitates such processes. (ii) The energetics of degradative processes may change after the first bond rupture, and in particular the possibility of autocatalytic degradation is ignored [78]. (iii) Ladder polymers are more rigid than single-chain structures. Flexibility of completely ladder polymers can result only from microdeformations of the macromolecular lattice (i.e. deformations of valence angles and bonds) during its thermal vibrations [79,80]; the great rigidity of ladder polymers hinders the development of concerted movements of the segments—even at very high temperatures—which significantly retards the start of degradative processes [81,82]. (iv) Development of the "cage effect" [83,84] involves retention in the vicinity of the radicals formed after rupture of any bond, which can thus readily recombine after the excess of energy has been dissipated: the construction of ladder polymers from aromatic systems leads after rupture to more ready restoration of the original structure [64,72].

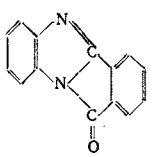
The empiricism of Tessler's scheme is still more evident when we pass from abstract double-chain systems to actual polymers. In particular, one of the principal postulates underlying the scheme—the equal strength of all bonds—is in effect impossible in polyheteroarylenes. Violation of this postulate, of course, nullifies a random character for degradation, and results in its preferential occurrence at the weakest bonds [1,3]. Thus a double-chain structure does not yet guarantee enhanced thermal stability in comparison with single-chain polymers, so that improved thermal characteristics in relation to traditional polyheteroarylenes cannot be expected from all ladder polyheteroarylenes, but only from those from which weak bonds are definitely absent.

Quantum-chemical calculations on several model compounds of ladder polyheteroarylenes and study of their degradation [85-88] have convincingly demonstrated significant differences in stability to thermal and thermohydrolytic degradation between models of different types of ladder polyheteroarylenes. In particular, 1,2-1',8'-naphthoylenebenzimidazole (I) and 2-phenylbenzimidazolo-[1,2-*c*]quinazoline (II)



(I) (II)

undergo degradation at temperatures 75 deg above that at which degradation of 1,2-benzoylenebenzimidazole (III)



(III)

begins [86,87]. Still more significant differences have been observed in the degradation of the polymers modelled by the above compounds and of other ladder polyheteroarylenes [88]. These differences are so considerable (up to 100–150 deg) that it is evidently inappropriate to speak of the thermal stability of ladder polyheteroarylenes as a whole.

Analysis of published results—extremely contradictory and frequently not comparable—nevertheless indicates that in several cases ladder polyheteroarylenes appreciably surpass traditional heterocyclic polymers in thermal stability. Thus ladder polyquinoxalines obtained by Stille et al. [89-91] begin to decompose, according to dynamic thermogravimetric analysis, in air at 550°C, but in an inert atmosphere at 700°C (Fig. 1). Polynaphthoylenebenzimidazoles exhibit high thermal stability [82,92-99], in full agreement with quantum-chemical calculations and results of a study of the degradation of model compounds [85-88]: under conditions of dynamic thermogravimetric analysis polymers of this type begin to decompose in air at 550°C, but after isothermal aging in air at 316°C for 500 h they retain 60–90% of the initial weight depending on structure [100] (Fig. 2). Polybenzimidazoloquinazolines possess still greater thermal stability, appreciably surpassing polynaphthoylenebenzimidazoles under conditions of isothermal thermogravimetric analysis [101] (Fig. 3). Under conditions of dynamic thermogravimetric analysis polybenzobispyrimidobenzimidazoles occupy an intermediate position between ordinary polyheteroarylenes and graphite [102] (Fig. 4), but under isothermal conditions they undergo no appreciable loss in weight on prolonged heating in air at 400°C. All the polyheteroarylenes examined are characterised not only by highly stable model compounds but also by high degrees of cyclisation. Thus polynaphthoylenebenzimidazoles are nearly 100% cyclised [92,100,103,104],

while polybenzimidazoloquinazolines and polybenzobispyrimidobenzimidazoles are 95% cyclised[105].

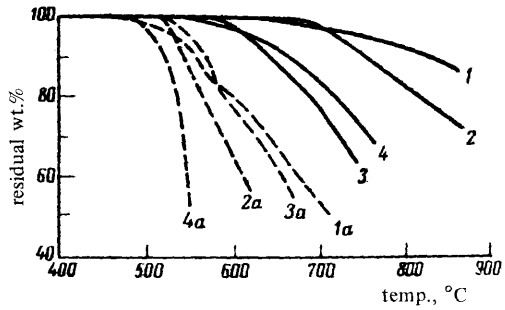
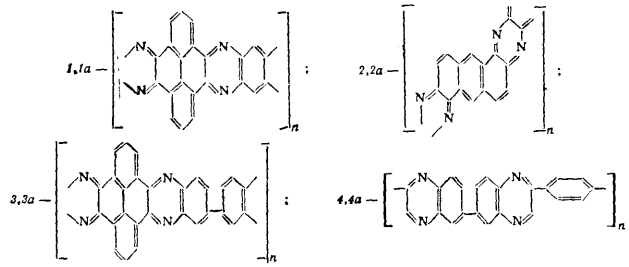


Figure 1. Dynamic thermogravimetric analysis curves (ΔT = 5 deg min^{-1}) in: 1)–4) an inert atmosphere; 1*a*)–4*a*) air for the polyquinoxalines:



Apart from ladder polyheteroarylenes possessing exceptionally high thermal stability several polymers of the same type are known whose thermal characteristics either do not surpass or are inferior to those of traditional polyheteroarylenes[106]. Some authors explain the low thermal stability of such ladder polymers either by the presence of readily decomposed groups[107] or by low thermal stability of the heterocycles forming the macromolecular double chain[108,109]. In the majority of cases, however, investigators are inclined to attribute inadequate thermal characteristics to structural defects[92,93,106,110,111], etc. to the heterounit character of the polyheteroarylenes[112–115]. This explanation is used especially frequently to interpret the unsatisfactory thermal stability of polybenzoylenebenzimidazoles, better known as "pyrrones"[92, 93,106,110–117]. The degree of cyclisation of pyrrones is indeed low (≤ 70%), which is confirmed both by experimental results[92,118,119] and by logical computations based on the complicated progress of a model reaction yielding together with the required 1,2-benzoylenebenzimidazole a wide range of products[76,77,120–123], as well as by the difficulties of solid-phase cyclisation in rigid polymer chains[93,124].

The heterounit character of pyrrones is responsible for their low thermal stability and leads in particular to the lower resistance of these polymers to degradation in comparison with the corresponding model compounds[116,117]. However, one deduction that may be made from this premise, formulated as "production of a polybenzoylenebenzimidazole of 100% (or simply a high degree of) cyclisation should yield a polymer of very high thermal stability", seems unsound, since compounds modelling pyrrones are characterised by comparatively low stability under conditions of thermal and thermohydrolytic degradation[85–88], in good agreement with earlier results[125–132] and with the high electrophilic reactivity of bis-1,2-benzoylenebenzimidazoles[133–135]. A similar principle applies also to other classes of ladder polyheteroarylenes having low degrees of cyclisation.

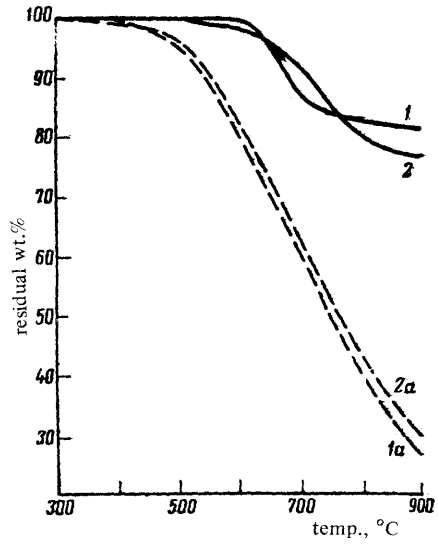
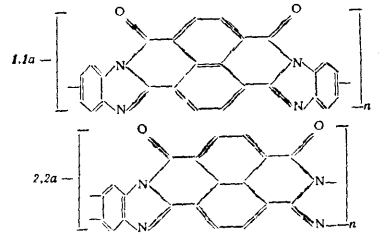


Figure 2. Dynamic thermogravimetric analysis curves (ΔT = 5 deg min^{-1}) in: 1), 2) air; 1*a*), 2*a*) an inert atmosphere for the polynaphthoylenebenzimidazoles



The heterounit character of ladder polyheteroarylenes is in principle closely connected with the stability of the heterocycles towards thermohydrolytic degradation and the action of various reagents, since the least stable heterocycles readily undergo all kinds of secondary reactions, tending to intensify the heterounit character of the polymers.

The high thermal stability of several of the above ladder polyheteroarylenes—polyquinoxalines, polynaphthoylenebenzimidazoles, polybenzimidazoloquinazolines, and polybenzobispyrimidobenzimidazoles—is apparent not only in higher temperatures at which they start to lose weight than for traditional polyheteroarylenes but also higher coking values, which in turn are closely related to the enhanced flame resistance of the polymers[136]. Ladder polymers possess considerably higher flame resistance

than traditional polyheteroarylenes: their oxygen indices exceed 0.6, in comparison with 0.3–0.45 for the latter.

Isolated experimental results indicate that ladder systems have a higher ablation resistance than traditional polyheteroarylenes. Polynaphthoylenebenzimidazoles[137,138] and polynaphthoylene-1,2,4-triazoles[139] possess especially high ablation resistance. Some workers[140–142] have noted considerable superiority of ladder polyheteroarylenes, in particular polyaroylenebenzimidazoles, in radiation resistance.

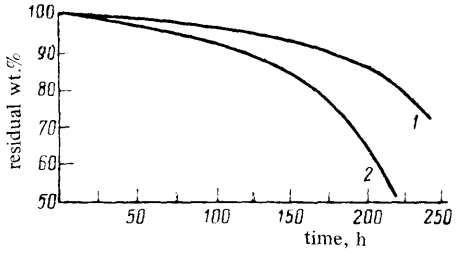
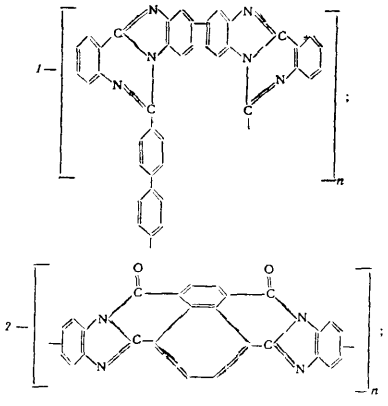


Figure 3. Isothermal thermogravimetric analysis curves in air at 361°C for: 1) polybenzimidazoloquinazolines; 2) polynaphthoylenebenzimidazoles:



Ladder systems are indisputably superior to the usual polyheteroarylenes in heat resistance. As a consequence of the great rigidity of polyheteroarylenes having a completely ladder structure their softening points are usually higher than the temperatures at which they begin to degrade. Even saturation by "hinge" groups of the main chains in partly ladder polyheteroarylenes rarely lowers their softening points below 400°C.

Significant advantages of ladder polyheteroarylenes have been found also in studying the working ranges of polynaphthoylenebenzimidazoles, polynaphthoylene-1,2,4-triazoles, polybenzimidazoloquinazolines, etc. Comparison with the corresponding ranges for traditional heterocyclic polymers[143] indicates the considerable superiority of ladder systems both in temperature and in strength parameters: ladder polyheteroarylenes are intermediate between ordinary polyheteroarylenes and sodium or potassium silicate glasses (Fig. 5).

Even the above far from complete analysis shows convincingly the considerable superiority of several ladder polyheteroarylenes over traditional heterocyclic systems in thermal stability and in heat, flame, radiation, and ablation resistance. Such superiority is due to highly stable heterocyclic groups in the macromolecules and also to close approach by the actual polymers to their ideal structures. The former factor is governed by the chemical structure of the polymers, whereas the latter largely depends on the method of synthesis of the polyheteroarylene.

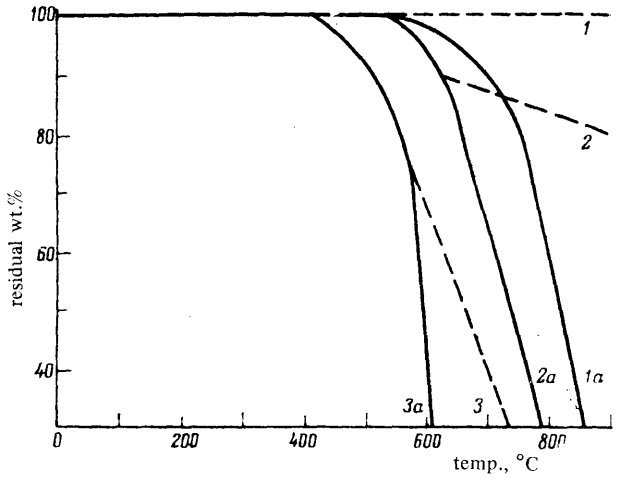
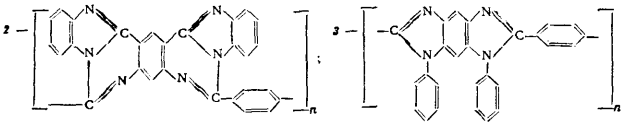


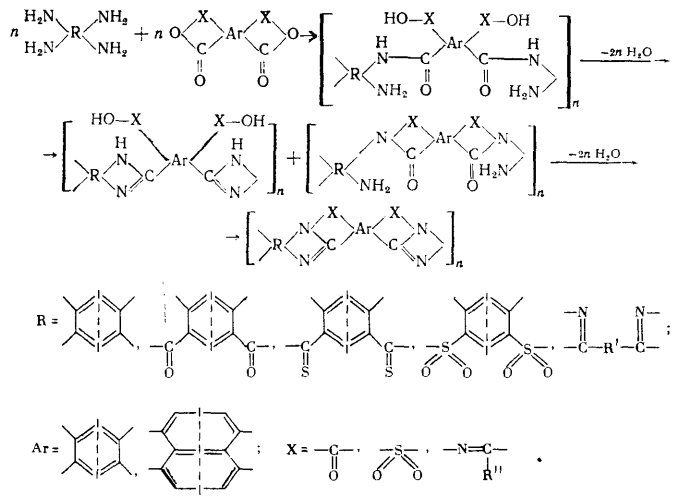
Figure 4. Dynamic thermogravimetric curves (ΔT = 5 deg min^{-1}) in: 1)–3) an inert atmosphere; 1*a*)–3*a*) air for: 1) graphite; 2) polybenzobispyrimidobenzimidazoles; 3) poly-*N*-phenylbenzimidazoles:



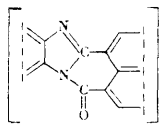
III. PRINCIPAL METHODS OF SYNTHESIS

Most ladder polyheteroarylenes are obtained by multifunctional polycondensation, primarily by condensation polyheterocyclisation[72]. The synthetic reactions involved in this form of the process can be divided into three main groups[76]: (1) three-stage reactions of aromatic tetracarboxylic acids, their derivatives or analogues, with tetrafunctional nucleophilic reagents containing four amino-groups in the form of amine, amide, hydrazide, and other fragments[76]; (2) two-stage reactions of aromatic dicarboxylic acids or their derivatives with aromatic diamines containing in *ortho*-positions aromatic heterocycles with labile hydrogen atoms; and (3) two-stage homo- or co-polyheterocyclisations of tetrafunctional monomers containing the functional groups in pairs with *ortho*, *α*, or *peri* mutual orientation.

(1) The three-stage process is a logical continuation and development [76] of two-stage polyheterocyclisation yielding polyimides, which can be represented by the formalised and generalised scheme



Little has changed in this field since a recent detailed review of this process [76], and fundamental investigations confirming the earlier tendency [76] have been made on the synthesis and technology of polynaphthoylenebenzimidazoles of general formula



obtained by the polycyclocondensation of bis-*o*-phenylenediamines with bis-(naphthalic dianhydrides). Among these a noteworthy development is a method for synthesising polynaphthoylenebenzimidazoles of high molecular weight with high degrees of cyclisation by high-temperature catalytic polycyclocondensation in an organic solvent [144], which enables the polymers to be obtained as finely divided powders. Novel polynaphthoylenebenzimidazoles soluble in phenolic solvents have been obtained from bis-3,4-diaminophenylhexafluoropropane. [145] In addition, polynaphthoylenebenzimidazoles can be obtained from dianhydrides other than naphthalene-1,4,5,8-tetracarboxylic, namely, 4,4′-dinaphthalic anhydride [146] and 8,8′-biquinolyl-4,4′,5,5′-tetracarboxylic dianhydride [147]. Besides this synthetic work research has been aimed at improving traditional methods for obtaining polynaphthoylenebenzimidazoles in acidic solvents, by developing the method of synthesis without waste in Lewis acids [148] and by supercooling under special conditions to obtain polymers of large surface area [149]. Most probably pure and applied research on the manufacture of polynaphthoylenebenzimidazoles will remain in the near future the main lines of development of the three-stage method for the synthesis of ladder polyheteroarylenes.

(2) The first of the above two-stage processes was developed by Korshak and his coworkers [150,151] in the search for optimum methods of synthesising polybenzimidazoloquinazolines and poly-1,2,4-triazoloquinazolines, for which the three-stage method does not give satisfactory results [76]. The two-stage method [150,151] is a logical development of the general synthesis of polybenzazoles [44-46] based on the two-stage reaction of aromatic dicarboxylic acids or their derivatives with aromatic diamines containing simple substituents such as hydroxy, mercapto, amino, phenylamino, etc. *ortho* to the amino-groups. The first stage involves formation of aromatic polyamides containing these substituents *ortho* to the amide links. In the second stage these *ortho*-substituents react with the amide groups to form benzazole heterocycles.

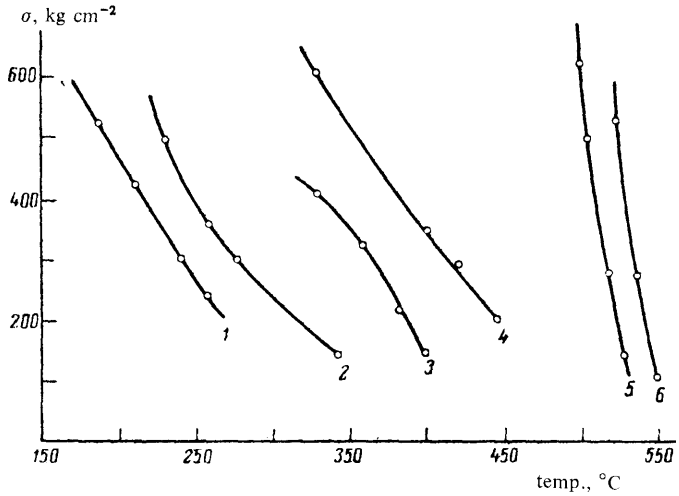
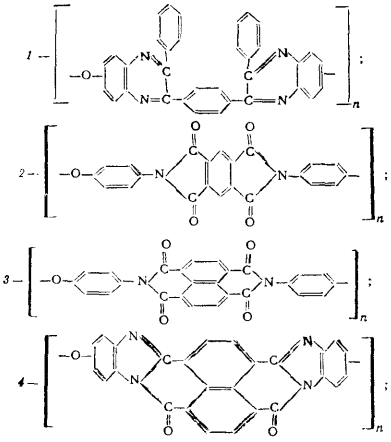
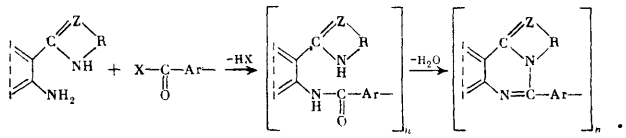


Figure 5. Working ranges of traditional polyheteroarylenes, ladder polyheteroarylenes, and glasses:

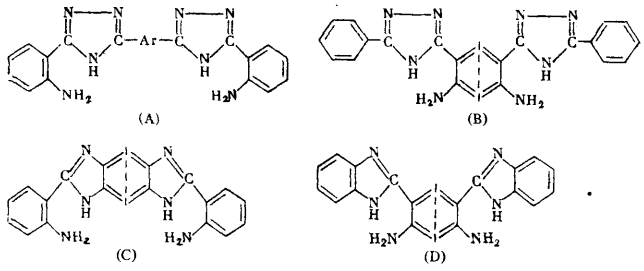


5) sodium silicate glass; 6) potassium silicate glass.

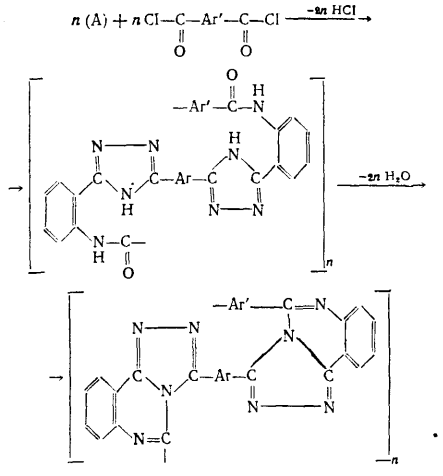
When diamines containing aromatic heterocycles in *ortho*-positions are used as monomers, the reactions follow a similar course, except that highly fused aromatic heterocycles are formed as a result of polycyclodehydration, and yield a partly ladder structure in the polyheteroarylenes obtained:



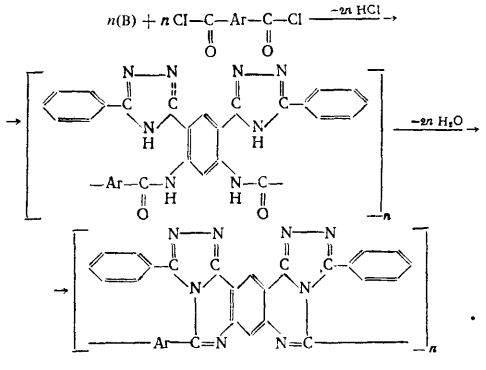
Among heterocycles that could potentially be used as *ortho*-substituents in the aromatic diamines the most widely used have been benzimidazole and 1,2,4-triazole rings:



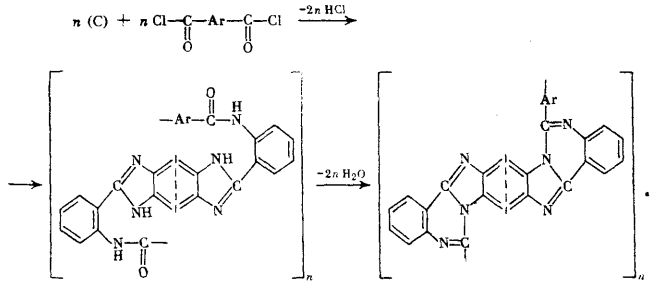
All four types of diamines have been used to obtain polyheteroarylenes of partly ladder structure. Diamines of type (A), bis-5-*o*-aminophenyl-1,2,4-triazol-3-ylarylenes, have given poly-1,2,4-triazoloquinazolines.[152-157] The most widely used synthesis of these polymers has been based on the two-stage method of mild interaction of the diamines with aromatic acid dichlorides in hexamethylphosphoramide followed by thermal cyclodehydration of the resulting poly-*o*-acylaminophenyltriazoles:



Under analogous conditions diamines of type (B), 4,6-di-(5-phenyl-1,2,4-triazol-3-yl)-1,3-phenylenediamines, have been treated with aromatic acid dichlorides to yield polybenzobistriazoloquinazolines of partly ladder structure[102,158,159]:



The same method of synthesis has been used to obtain partly ladder polyheteroarylenes from diamines of types (C) and (D). The action of acid dichlorides on 2,2'-di-*o*-aminophenylimidazolobenzimidazoles has given polybenzimidazoloquinazolines[150,151,160-166]:

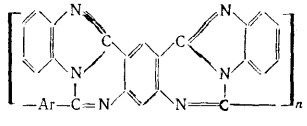


When diamines of type (D) are used as initial compounds, polybenzimidazoloquinazolines[160,167] and polybenzobispyrimidobenzimidazoles[102,158-160,168,169] are obtained.

Single-stage processes—polycyclocondensation in the melt with the use of diphenyl dicarboxylates[101,166,179,171] and high-temperature polycyclocondensation in polyphosphoric acid—can also be employed to obtain the above polymer systems. With triphenyl tricarboxylates as monomers "cross-linked" polybenzimidazoloquinazolines are obtained[101,171,172].

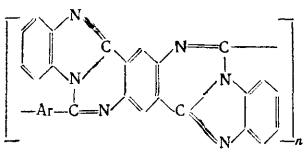
All the polyheteroarylenes obtained by the present method are closely similar in properties, both in the prepolymer stages and in the final stages. Depending on the specific structure of the prepolymers—copolyamidobenzimidazoles and copolyamido-1,2,4-triazoles, as well as polyamides containing *o*-benzimidazolyl and *o*-triazolyl substituents—they exhibit either limited solubility or complete insolubility in bipolar aprotic solvents. These polymers are characterised by comparatively low molecular weights (up to 30 000), probably because of the relatively weak nucleophilic character of the initial diamines containing bulky shielding substituents *ortho* to the amino-groups. The required partly ladder polymers are soluble only in strong acids such as sulphuric, trifluoroacetic, polyphosphoric, etc. These systems possess high heat resistance and thermal stability: under conditions of dynamic thermogravimetric analysis in air many of these polymers undergo no loss in weight right up to 500°C.

The greatest thermal stability is shown by polybenzobispyrimidobenzimidazoles

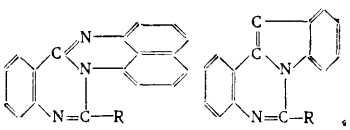


which are formed by the action of aromatic acid dichlorides on 4,6-bisbenzimidazol-2'-yl-1,3-phenylenediamine. The high thermal stability of these systems is probably due not only to stability of the heterocycles and high degrees of cyclisation of the polymers but also to absence of isomerism in the heterocycle, which according to Marvel[173] should influence favourably the thermal properties of polymers. For comparison we note that ladder polyheteroarylenes obtained by the three-stage method[76] contain a large quantity of structural isomers even in the ideal completely cyclised structures. Perhaps the thermal stability of polybenzobispyrimidobenzimidazoles

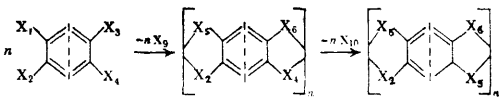
can be further enhanced by passing to more regular structures [173], e.g.



Diamines containing perimidine, indole, pyrrole, and other groups *ortho* to the amino-groups can also be used as monomers. This is supported by published results on the formation of the model compounds [174,175]

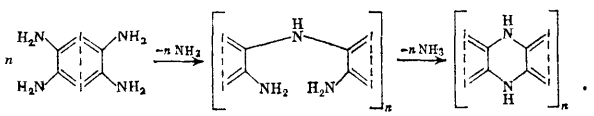


(3) The second of the above two-stage methods is the most widely used for the synthesis of partly or completely ladder polyheteroarylenes containing aromatic or hydroaromatic six-membered heterocycles. The general scheme of homocondensation can be written



where X_1–X_4 are the same or different functional groups, which differ from the groups X_5–X_8 by the molecules of the condensation by-products X_9 and X_{10}.

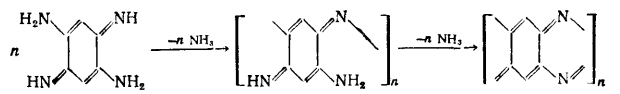
The simplest reactions of this type, in which $X_1 = X_2 = X_3 = X_4$, involve the homocondensation of bis-*o*-phenylenediamines [176–178] in polyphosphoric acid at 250–350°C:



The reaction products are polydihydrophenazines, which can undergo partial oxidation of quinoxaline fragments. The polymers obtained possess high thermal stability (that from bis-3,4-diaminophenyl ether loses only 14% of its initial weight when heated in nitrogen to 900°C). However, their thermo-oxidative stability is considerably lower (owing to the presence of the NH groups); they have limited solubility in sulphuric and methanesulphonic acids, and poor viscosity characteristics (specific viscosity 0.2–0.4 dl g^{-1}).

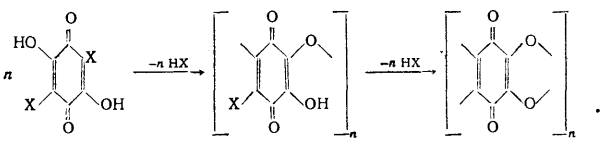
Polymers of closely similar structure have been synthesised by the homocondensation of 6,7-diaminoquinoxaline-2,3-diol in polyphosphoric acid [179]. The presence of imino-groups in the resulting polyquinoxalinodihydrophenazines is responsible for their relatively low resistance to thermal oxidation in comparison with the above polydihydrophenazines. An attempt at a fundamental improvement in the solubility and stability of the polymers by replacing hydrogen atoms in the dihydrophenazine rings with phenyl groups by using bis-*N*-phenyl-*o*-phenylenediamines as monomers did not yield the desired poly-*NN'*-diphenyldihydrophenazines [180].

A rather more successful attempt to use the homocondensation of tetrafunctional monomers to produce completely aromatic ladder polyheteroarylenes was made with 2,5-diamino-1,4-benzoquinonedi-imide in polyphosphoric acid [181]:



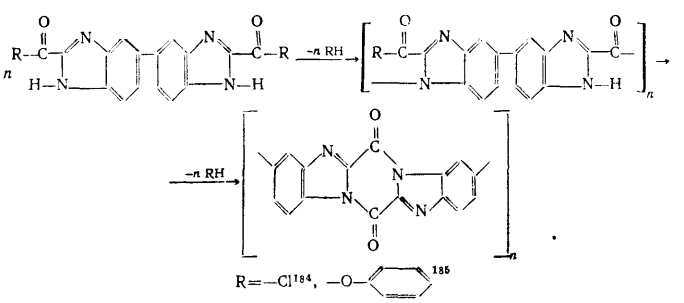
The resulting polymers have high thermal stability: weight losses associated with the start of degradation are observed at 450–480°C, while the most thermostable specimens lose 5% and 19% at 600 and 900°C respectively. Nevertheless, the products of homocondensation have only limited solubility in sulphuric acid and exhibit very poor viscosity characteristics (specific viscosity not exceeding 0.05 dl g^{-1}).

Other derivatives of *p*-benzoquinone have attracted the attention of research workers. In particular, Berlin et al. [182,183] accomplished the homocondensation of chloro- and bromo-anilic acids to polyquinonedioxins:



The synthesis of polyquinonedioxins in the melt [182] and in biphenyl, dimethylformamide, and *N*-methylpyrrolid-2-one [183] gives intensely coloured products of low molecular weight, characterised by sparing solubility and poor thermal stability. Thus these polymers lose up to 50% of their initial weight when heated in an inert atmosphere to 400°C for a few hours.

The homocondensation of derivatives of 5,5'-bibenzimidazolyl-2,2'-dicarboxylic acid [184,185] differs somewhat from the above reactions:

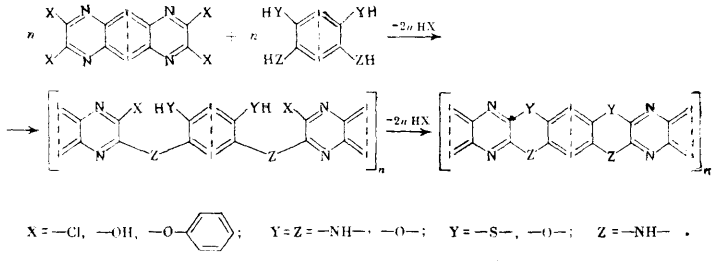


The mobile hydrogen atom of the benzimidazole ring acts as a functional group involved in polyheterocyclisation. Homocondensation of the acid dichloride was effected in thionyl chloride [184], and that of the diphenyl ester in the melt or in thiolan *S*-dioxide [185]. The resulting polybisbenzimidazopyrazinediones are partly soluble in sulphuric and methanesulphonic acids, have $[\eta] = 0.15$–0.62 dl g^{-1}, and according to thermogravimetric data begin to decompose in an inert atmosphere and in air at 465 and at 350–400°C respectively.

Inspection of the above results indicates that most ladder polyheteroarylenes obtained by the homocondensation of tetrafunctional monomers possess comparatively low molecular weights, limited solubility, and comparatively low (especially under conditions of thermal oxidation) temperatures at which degradation begins, which in combination present considerable difficulties to the use of

these polymers as foundations for thermostable materials. Another noteworthy feature is the limited range of tetrafunctional monomers used in homocondensation processes.

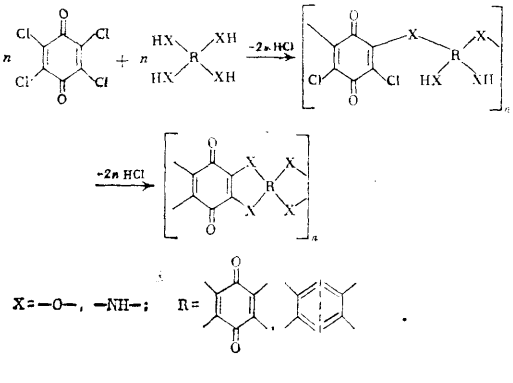
A considerably wider range of monomers can be used in the polycyclocondensation of two different tetrafunctional monomers. Marvel et al.[178,186-196] have made a comprehensive investigation of the reactions of tetrasubstituted bisquinoxalines and tetra-aza-anthracenes containing activated halogen, hydroxyl, and phenoxyl groups with bis-*o*-phenylenediamines, bis-*o*-aminophenols, bis-*o*-aminothiols, and tetraphenols. These processes can be represented by the general scheme



X = —Cl, —OH, —O—⟨benzene⟩; Y = Z = —NH—, —O—; Y = —S—, —O—; Z = —NH— .

The polymers can be synthesised in the melt or by high-temperature polycyclocondensation in an organic solvent of high boiling point or in polyphosphoric acid. They contain alternating quinoxaline and dihydrophenazine, oxazine, thiazine, and dioxin rings. They possess comparatively high thermal stability (dynamic thermogravimetric analysis indicates that their degradation begins at 450–550°C), but relatively low molecular weights and limited solubility, which presents considerable difficulties when they are processed into articles.

Although various groups can be used as functions in tetrasubstituted bisquinoxalines and tetra-aza-anthracenes, tetrachloro-derivatives have been most commonly employed, in which the chlorine atoms are highly reactive. Such derivatives have found the widest use also in another group of monomers—derivatives of *p*-benzoquinone—from which ladder polyheteroarylenes are obtained[197,198]. The general scheme of reaction of these compounds with tetrafunctional monomers can be represented

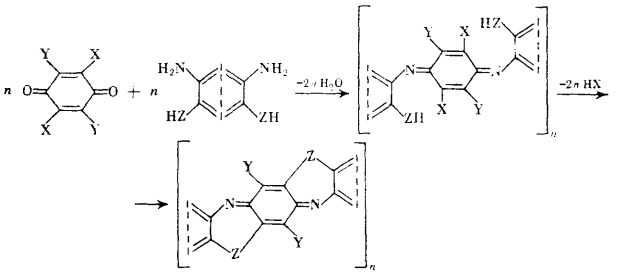


X = —O—, —NH—; R = ⟨quinone⟩ .

Polymers analogous in structure to products of the homocondensation of chloro- and bromo-anilic acids are obtained by reaction between chloranil and tetrahydroxy-*p*-benzoquinone[197]. The resulting polyquinonedioxins are intensely coloured substances of comparatively low molecular weight, identical in properties with products of the homocondensation of chloro- and bromo-anilic acids.

Polymers very similar in properties to polyquinonedioxins are obtained by the action of chloranilic acid or chloranil on bis-*o*-phenylenediamines[198].

In the above syntheses of ladder polyheteroarylenes the carbonyl groups of *p*-benzoquinone are not involved in polycyclocondensation but remain in the final macromolecular structures. A somewhat different approach was made by Stille and by Marvel[108,109,181,199-202], who achieved the polycyclocondensation of *p*-benzoquinone derivatives with various monomers in which the carbonyl groups of the former were involved in ring formation:



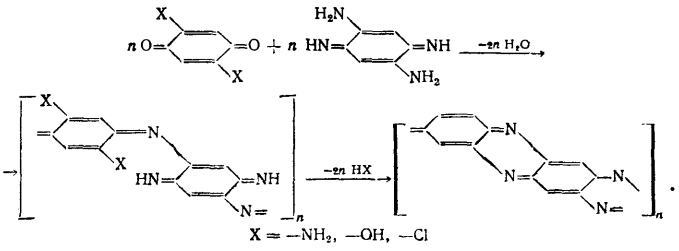
X = —OH, —O.CO.CH$_3$, —NH$_2$, —Cl; Y = —H, —Cl; Z = —O—, —NH—, —S— .

Thus polyphenoxazines of high molecular weight were obtained by reaction of bis-*o*-aminophenols with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone and with its diacetate[108,109]. The chief defects of these polymers are limited solubility in organic solvents and low thermal stability (in nitrogen a loss in weight was observed at 250–275°C), the latter due, as already noted, to the low thermal stability of the phenoxazine ring[108,109].

Polymers of great interest with respect to thermal stability have been obtained by the reaction of 2,5-dihydroxy-, 2,5-dichloro-, and 2,5-diamino-1,4-benzoquinones with bis-*o*-phenylenediamines[199-201]. In the case of the diol polycyclocondensation was accomplished in dimethylacetamide, hexamethylphosphoramide, and polyphosphoric acid; the polymers obtained in hexamethylphosphoramide were completely soluble in this solvent and possessed an intrinsic viscosity of 0.60–1.40 dl g^{-1}. Polydihydrophenazines obtained in dimethylacetamide and polyphosphoric acid are 50% and 30% soluble in hexamethylphosphoramide, and possess intrinsic viscosities of 0.57 and 1.45 dl g^{-1} respectively. The polymers begin to decompose in air and in nitrogen at 525 and 535°C respectively.

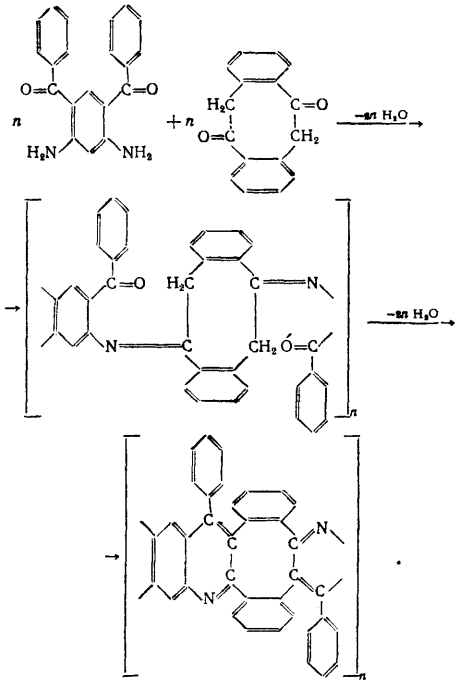
Analogous polymers have been obtained with 2,5-diamino- and 2,5-dichloro-1,4-benzoquinones[199-201]. Marvel et al.[202] obtained a polytriphenodithiazine from the reaction of 2,5-dichloro-1,4-benzoquinone with the dihydrochloride of 4,4′-diaminobiphenyl-3,3′-dithiol. Continuing the reaction in dimethylacetamide at 150°C for 24 h gave a polymer of low molecular weight having a specific viscosity of 0.12 dl g^{-1}, soluble only in sulphuric acid. The same process in polyphosphoric acid gave a polymer that was partly soluble in sulphuric acid (specific viscosity 0.54 dl g^{-1}). Dynamic thermogravimetric analysis in helium indicates that the polymer loses 3% of its initial weight at 500°C.

Polymers of completely ladder structure have been obtained by the reaction of 2,5-diamino-, 2,5-dihydroxy-, and 2,5-dichloro-1,4-benzoquinones with 2,5-diamino-1,4-benzoquinonedi-imide in polyphosphoric acid[181]:

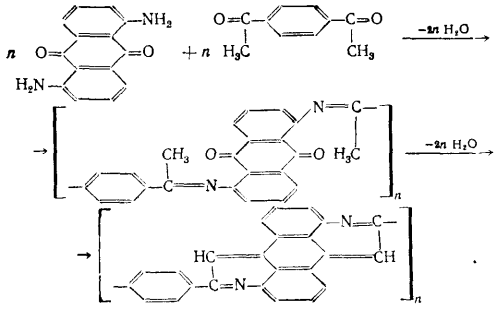


Dynamic thermogravimetric analysis in nitrogen showed that the resulting polyphenazines possess comparatively high thermal stability, comparable with that of products of the homocondensation of 2,5-diamino-1,4-benzoquinone-di-imide. The ladder polyphenazines have the defects of poor solubility (they are only partly soluble in sulphuric acid) and comparatively low viscosity characteristics (specific viscosity ≤ 0.2 dl g^{-1}).

Extending the Friedländer and related processes to the synthesis of macromolecular compounds is of considerable interest for the production of novel polyheteroarylenes of partly and completely ladder structure[203-205]. In particular, Stille et al.[204] have obtained a polymer of ladder structure from 4,6-dibenzoyl-1,3-phenylenediamine and a cyclic bisketomethylene compound—dibenzo[*a*,*e*]-cyclo-octene-5,11(6*H*, 12*H*)-dione:

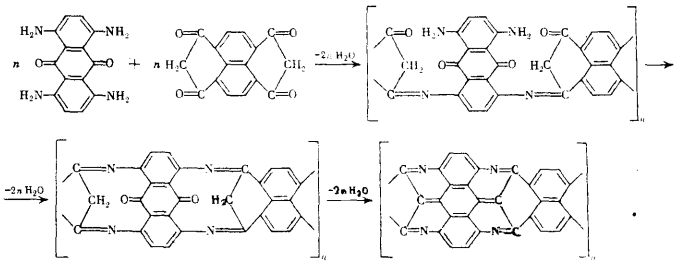


A process related to the Friedländer reaction has been used[206] to obtain a partly ladder polybenzodiquinoline from 1,5-diaminoanthraquinone and a series of diacetylated aromatic compounds. Most interesting results are obtained with *p*-diacetylbenzene[206]:



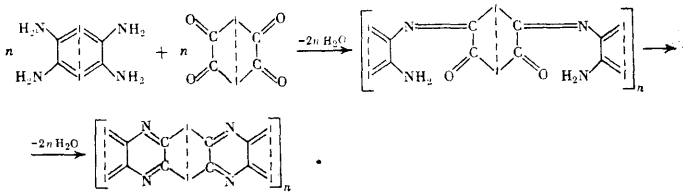
The first stage, effected in the melt at 240°C for 30 min, gives a polymeric Schiff base soluble in sulphuric and methanesulphonic acids, having a specific viscosity of 0.46 dl g^{-1}. The second stage occurs when the polymer is heated in polyphosphoric acid at 150°C for 5 h. Dynamic thermogravimetric analysis indicates that the resulting polybenzodiquinoline begins to decompose in air at 440°C, but in nitrogen it loses only 10% of its initial weight at 900°C.

Further development of this line of attack led to the synthesis of a graphite-like polymer[207-209] from 1,4,5,8-tetra-aminoanthraquinone and 1,2,3,6,7,8-hexahydropyrene-1,3,6,8-tetraone. It would be more correct to regard this not as a two-stage polycyclocondensation of two tetrafunctional monomers but as a three-stage polycyclocondensation of two hexafunctional compounds:



Interaction of the initial compounds in polyphosphoric acid at 170°C for 20 h gave a polymeric Schiff base soluble in sulphuric acid, with specific viscosity 2.7 dl g^{-1}. Subsequent vacuum treatment at 340°C for 2–5 days yielded the required highly condensed system. Isothermal thermogravimetric analysis in circulating air indicated appreciable weight losses even at 300°C, probably largely owing to the low degree of cyclisation of the system. An interesting feature of the polymer is its high electrical conductivity of 2×10^{-4} ohm^{-1} cm^{-1}.[210]

Examination of the literature indicates that the reaction most often used in the synthesis of ladder polyheteroarylenes is the condensation of amino and carbonyl groups. The same reaction forms the basis of the synthesis of ladder polyquinoxalines[89-91,107,204,211]:



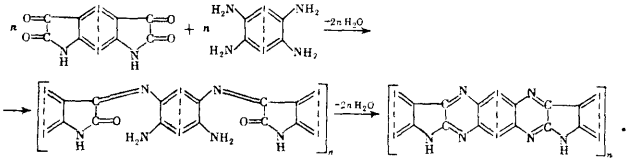
Using 3,3,6,6-tetramethylcyclohexane-1,2,4,5-tetraone as tetracarbonyl compound, Stille et al.[107] obtained polyquinoxalines of comparatively low thermal stability resulting from the ease of decomposition of the isopropylidene groups. In air the polymers began to break down at 200–290°C depending on their structure, but in an inert atmosphere at 400°C.

Completely aromatic ladder polyquinoxalines were obtained by the use of pyrene-1,2,6,7-tetraone and anthracene-1,2,6,7-tetraone as initial tetracarbonyl compounds, and of benzene-1,2,4,5-tetra-amine, naphthalene-1,2,5,6-tetra-amine, 1,2,5,6-tetra-aminoanthraquinone, and dibenzo-*p*-dioxin-2,3,6,7-tetra-amine as the initial bis-*o*-phenylenediamines[89-91].

Thus the reaction of benzenetetra-amine with pyrene- and anthracene-1,2,6,7-tetraones in hexamethylphosphoramide at 180°C for 120 h gave completely aromatic polyheteroarylenes, which would have been more correctly termed not polyquinoxalines but polytetra-aza-anthracenes[89]. These polymers did not dissolve in cold hexamethylphosphoramide, but were completely soluble in dichlorotetrafluoroacetone hydrate. The specific viscosities of the polymers reached 2.1 dl g^{-1}, corresponding to molecular weights of 7000–15 000. Still higher molecular weights were obtained by synthesising the polymers in polyphosphoric acid: the above polytetra-aza-anthracenes had specific viscosities up to 3.6 dl g^{-1}. Such polymers are characterised by *syn–anti* isomerism in the macromolecular chains, which enhances their solubility and processability into articles.

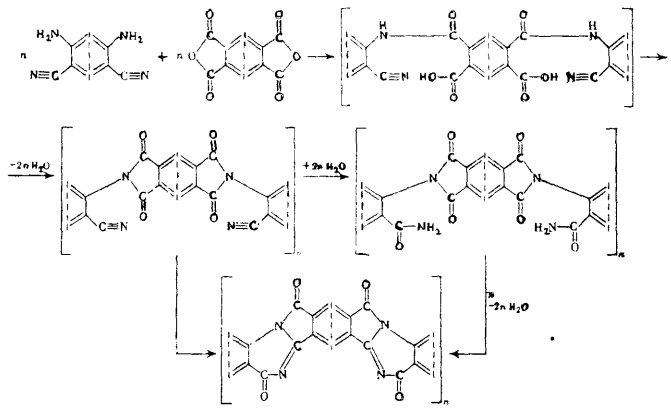
Several of the polymers possess film-forming properties. Dynamic thermogravimetric analysis indicates that the start of their degradation in air lies in the same temperature range as for linear polyquinoxalines (~550°C), but in an inert atmosphere the ladder systems exhibit considerably greater stability, beginning to decompose in the region of 700°C.

Bi-isatyls have also been used as tetraoxo-monomers: they react with bis-*o*-phenylenediamines to form polyindoloquinoxalines[212-219]:

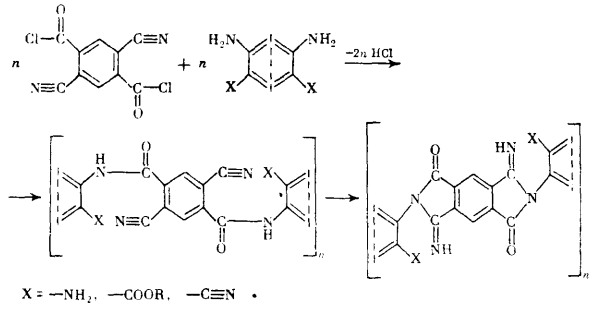


The synthesis of these polymers, like that of ladder polyquinoxalines, proceeds most smoothly in polyphosphoric acid, when the products are completely soluble in sulphuric and methanesulphonic acids with intrinsic viscosities up to 1 dl g^{-1}.[217-219] Dynamic thermogravimetric analysis indicates that these polymers begin to decompose at 460 and at 700°C in air and in nitrogen respectively[217-219].

All the aoove processes involve condensation polyheterocyclisation: i.e. they are accompanied by the evolution of volatile products of low molecular weight, which makes it difficult to obtain massive articles free from defects (pores, cracks, etc.). As a consequence, isomerisation cyclisation, which does not involve the formation of volatile products, is of considerable interest for the production of ladder polyheteroarylenes, as of heterocyclic polymers as a whole[220-224]. Ladder polyheteroarylenes have been most commonly synthesised from prepolymers containing nitrile groups, although by no means all the processes considered below involve purely isomerisation polycyclisation. Thus reaction between tetracarboxylic dianhydrides and bis-*o*-amino-nitriles forms poly-*o*-carboxy-*o'*-cyano-amides, cyclodehydration of which yields polyimides containing *o*-nitrile substituents; cyclisation of these polyimides in turn leads to poly-isoindoloquinazolinediones[225-227]:

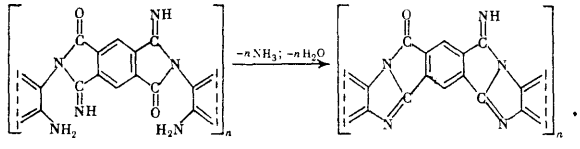


Several ladder polyheteroarylenes are obtained by thermal cyclisations of *ortho*-substituted poly-imino-imides[228]:



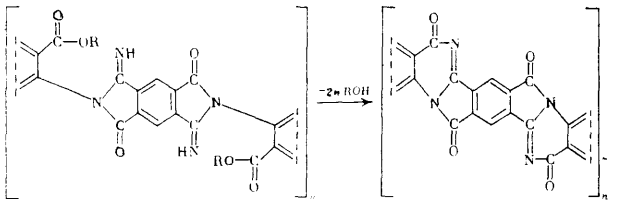
X = —NH_2, —COOR, —C≡N .

In some cases only intermediate *ortho*-substituted poly-iminoimides are formed by the isomerisation mechanism, and the concluding stage is accompanied by the evolution of simple products. Thus the reaction of hydrochlorides of aromatic tetra-amines with 2,5-dicyanoterephthaloyl chloride gives rise to poly-*o*-amino-*o'*-cyano-amides, heat-treatment of which at 150°C is accompanied by isomerisation cyclisation giving poly-*o*-amino-imino-imides. Heating these polymers at 250–350°C leads to the formation of polybenzoylenebenzimidazoles and their imino-analogues with the liberation of water or ammonia[229]:



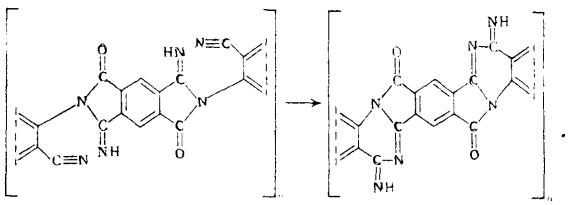
The resulting polymers are soluble in sulphuric acid, possess specific viscosities of ~0.5 dl g^{-1}, and according to thermogravimetric analysis lose 5% of their initial weight in air at 400°C. The comparatively low thermal stability is not surprising in view of the great activity of the 1,2-benzoylenebenzimidazole ring[76], also containing an exocyclic imino-group, which is undoubtedly the "weak spot" in these systems.

The action of 2,5-dicyanoterephthaloyl chloride on bisaniline-*o*-carboxylic acids or their methyl esters forms polyamides containing nitrile and carboxyl or methoxycarbonyl *ortho*-substituents. Isomerisation cyclisation of these systems at 130–150°C results in poly-iminoimides containing *o*-carboxyl or *o*-methoxycarbonyl groups and undergoing at 200–250°C cyclocondensation with the liberation of water or methanol and formation of polyisoindoloquinazolinediones [230]:



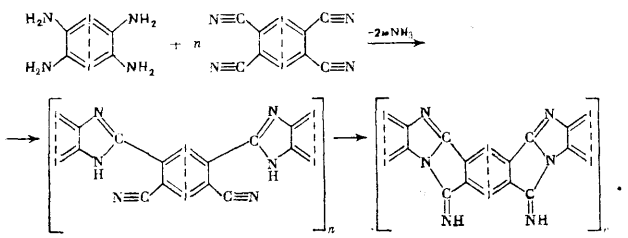
The resulting polymers are soluble only in sulphuric acid, possess specific viscosities up to 0.8 dl g^{-1}, and begin to undergo extensive degradation at 500°C.

Polyheteroarylenes of partly or completely ladder structure, which undergo cyclisation solely by an isomerisation mechansim, are obtained by reaction between 2,5-dicyanoterephthaloyl chloride and bis-*o*-aminonitriles followed by heat-treatment of the resulting poly-*oo'*-dicyano-amides with the temperature raised step by step to 300°C [231,232]:

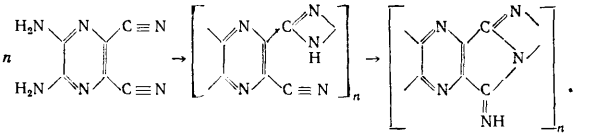


The poly-*oo'*-dicyano-amides formed in the first stage are readily soluble in polar organic solvents and possess sufficiently high molecular weights to form strong and flexible films. The final polyiminoisoindoloquinazolinediones begin to decompose at 400–450°C according to thermogravimetric data. Since the second stage of isomerisation cyclisation does not involve the separation of simple products, the resulting polymers can be processed into monolithic articles of considerable thickness or used as binders for glassfibre-reinforced plastics and for adhesives.

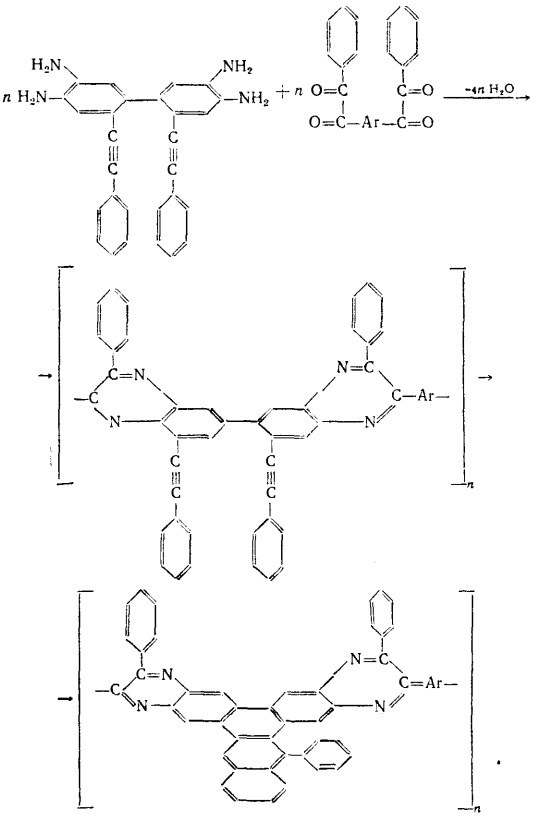
Polybenzimidazoles containing *ortho*-nitrile substituents can also undergo isomerisation cyclisation [233,234]. Thus the condensation of equimolecular quantities of tetranitriles with bis-*o*-phenylenediamines in boiling 2-methoxyethanol containing sodium 2-methoxyethoxide gives insoluble black polymers [233]:



Thermogravimetric analysis indicates that the polymer formed from biphenyl-3,3'-4,4'-tetra-amine and the tetranitrile of pyromellitic acid is the most thermostable, losing 10% of its weight respectively at 500 and 700°C in air and in argon. Still better thermal characteristics are attributed to the product of the homocondensation of 2,3-diamino-5,6-dicyanopyrazine [234]



Isomerisation cyclisation can be applied also to polymers containing ethynyl side-chains. A typical example of such intramolecular processes is the formation of condensed systems by the heat-treatment of polyphenylquinoxalines obtained from 6,6'-diphenylethynyl-biphenyl-3,3',4,4'-tetra-amine and various tetraones [235-238]:



The resulting phenylated polyanthrabisquinoxalines have high glass points combined with high degradation temperatures (respectively > 360 and ~450°C).

On the whole ladder polyheteroarylenes obtained by isomerisation cyclisation do not possess especially good thermal characteristics, but the advantages of the cyclisation process open up wide prospects before isomerisation cyclisation.

IV. PRACTICAL APPLICATION—ACHIEVEMENTS AND PROSPECTS

The most considerable achievement in the practical application of ladder polyheteroarylenes is the development of polynaphthoylenebenzimidazole fibres, obtained

by spinning sulphuric-acid solutions of these polymers[239-245]. After being stretched 80–120% at 525–600°C these fibres possess at room temperature a tensile strength of 5 g denier^{-1} and an extension at break of 5%. In air the fibres retain 55–60% of their strength after 1 min at 660°C and after 30 h at 360°C; they resist the action of moisture and ultraviolet radiation[243]. At the present day they are the most thermostable among organic fibres. Not only fibres but also thermostable films[246], composition materials[247-249], and several other materials have been obtained from polynaphthoylenebenzimidazoles.

Polybenzimidazoloquinazolines can form the basis for carbon plastics that retain good strength characteristics (bending strength 1080 kg cm^{-2}) at temperatures around 370°C,[101,170-172] and also for adhesives which maintain a high strength after being aged in air at 400°C.[250]

Ladder polyquinoxalines have been used as binders for glassfibre-reinforced plastics[252], but only fragmentary attention has been paid to the properties of these materials. Practical utilisation of ladder polyheteroarylenes—even the most heat-resistant and thermostable—is governed primarily by their poor processability into articles: the great rigidity of these ladder polymers is responsible for their high softening points, which often lie even above the temperatures at which decomposition begins. The same factor also causes the limited solubility of ladder polyheteroarylenes, most of which are soluble only in strong acids. Several approaches are now envisaged towards overcoming the poor processability of ladder polyheteroarylenes.

Among purely synthetic approaches an important place will probably be occupied by the above trend to diminish the rigidity of the macromolecules[145-147,254] by using new monomers containing single carbon–carbon bonds or "hinge" groups. However, this requires the development of novel monomers and careful selection of the most readily available among them. In this connection it seems more promising to prepare copolymers and make polymer mixtures[255]. In particular, considerable interest attaches to the production of random and block copolymers containing fragments of ladder polyheteroarylenes and no less thermostable polymers that appreciably surpass the former in processability, among which polyphenylquinoxalines present the greatest interest[256-258]. On the other hand, such production of copolymers of polyphenylquinoxalines and ladder polyheteroarylenes can be regarded as a method of enhancing the thermal stability of the former, an urgent problem in the chemistry of polyphenylquinoxalines[256-258]. Mixtures of traditional polymers with ladder polyheteroarylenes are still more promising, provided, of course, that the components show good compatibility. Small additions of ladder polyheteroarylenes to traditional polymers may lead to stabilisation[259] and "alloying"[260] of the latter, whereas the introduction of considerable quantities of ladder polyheteroarylenes can probably raise the temperature of prolonged operation of the polymeric materials to 300–350°C. The search for optimum forms of such mixtures of polymers is an extremely promising approach, since it may lead to relatively cheap thermostable polymeric materials.

V. CONCLUSION

The present survey enables us to assess the present situation in the chemistry of ladder polyheteroarylenes. Greater resistance to various types of degradation can be expected from partly and completely ladder polyheteroarylenes than from traditional polyheteroarylenes, provided that the heterocycles in the main chains are very stable and the polymers as highly cyclised. At the present time this potential advantage of ladder polyheteroarylenes has been realised only with a comparatively small number of systems—ladder polyquinoxalines, polynaphthoylenebenzimidazoles, polybenzimidazoloquinazolines, polybenzobispyrimidobenzimidazoles, and a few others—which meet both requirements formulated above.

A low degree of cyclisation is not adherent in all ladder polyheteroarylenes: high degrees can be achieved in such systems, but careful choice both of the reactions themselves and of the reaction conditions is necessary. The latter requirement is quite understandable, for the synthesis of ladder polyheteroarylenes (especially the three-stage process[76]) may involve the formation of various intermediate structures and lead to a wide range of end-products. As a consequence, processes that in the chemistry of individual (model) compounds give maximum yields of the required systems are to be preferred. There is no doubt that more careful selection of the processes involved in synthesis of ladder systems and careful selection of reaction conditions can lead to the appearance of novel polymers possessing enhanced stability to various types of degradation.

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Synthesis of Polymers by Polycyclotrimerisation

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Research on the synthesis and properties of cross-linked polymers obtained by a promising new method—polycyclotrimerisation of monomers containing acetylenic and multiple carbon-nitrogen bonds—is surveyed with attention concentrated mainly on recent studies of the laws governing the reaction, elucidation of the influence of the heterounit character of cross-linked systems on their properties, and the development of methods for effecting highly selective polycyclotrimerisation with the aim of diminishing the "defectiveness" of the polymers and obtaining molecularly regular networks. Characteristics of polycyclotrimerisation of monomers having various functional groups (C:CH, C:N, N:C:O, O.C:N, NH.C:N, NR.C:N) are identified, and the influence of the structure of the initial monomers on the properties of the resulting cross-linked polymers is examined. A list of 159 references is included.

CONTENTS

I. Introduction 79
II. Polycyclotrimerisation of acetylenic compounds 79
III. Polycyclotrimerisation of monomers with multiple carbon-nitrogen bonds 84

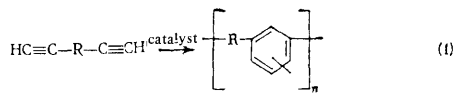
I. INTRODUCTION

Progress in the chemistry of macromolecular compounds results not only from the introduction of increasing numbers of novel monomers into known polymerisation reactions but also from the application and development of new synthetic methods. Investigations devoted to the latter occupy an important place in the work of Korshak and his pupils: for example, Korshak and Kolesnikov[1] discovered transarylation, and Korshak and Sosin[2] polyrecombination. Recently Korshak and his coworkers have been actively studying polycyclotrimerisation, a new reaction in polymer chemistry[3-7]. This process permits the synthesis of cross-linked polymers of regular chemical structure containing segments of definite size between cross-links, and six-membered carbocyclic and heterocyclic rings at the branch points: i.e. cross-linked polymers can be obtained of a qualitatively new standard in comparison with hitherto known synthetic methods for such systems.

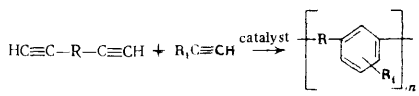
The present Review surveys the polycyclotrimerisation of monomers containing triple carbon-carbon and multiple carbon-nitrogen bonds— the two main types used for such synethses of cross-linked polymers.

II. POLYCYCLOTRIMERISATION OF ACETYLENIC COMPOUNDS

The new synthetic method is based on the cyclotrimerisation of various acetylenic compounds, a reaction known in organic chemistry[3]. When diacetylenic compounds or mixtures of diacetylenic with monoacetylenic compounds are used, the formation of polymers can be represented by the general schemes[8]



(1)



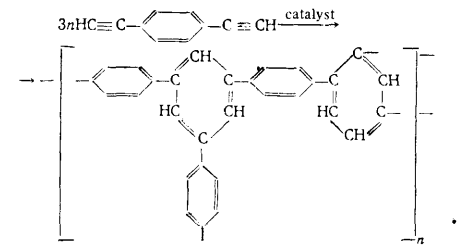
(2)

Polymer formation can thus be regarded as polycyclotrimerisation (1) or copolycyclotrimerisation (2). Such reactions had not previously been studied systematically with the aim of obtaining polymers. However, a considerable body of results have already been published on various cases of the polycyclotrimerisation of acetylenic compounds, which we can summarise in the light of the formation of polymeric products as a whole.

Conversion of acetylene into benzene, naphthalene, and other aromatic compounds at high temperatures (above 600°C) was first achieved by Berthelot[9] as early as 1866. Zelinskii[10] obtained high yields of aromatic hydrocarbons by passing acetylene over activated charcoal at 600–650°C. Studies were made[11-15] of the influence on the aromatisation of acetylenes of diverse catalysts–activated charcoal, kaolin, coke, alumina, quartz, china, pumice, brick, and also metals such as aluminium, iron, nickel, cobalt, etc.

The catalytic cyclotrimerisation of acetylenes was discovered by Reppe et al.[16,17] in 1940; it enabled high yields of products of diverse structure to be obtained under comparatively mild conditions. At the present time it is a process of great practical interest. The broad groups of catalytic systems used for the cyclotrimerisation of acetylenes comprise various complex organometallic catalysts, based e.g. on hydrides[18,19], salts[20-22], and π-complexes of metals[23,24], complexes of zerovalent metals[25], metal-oxide catalysts[26], and others[27].

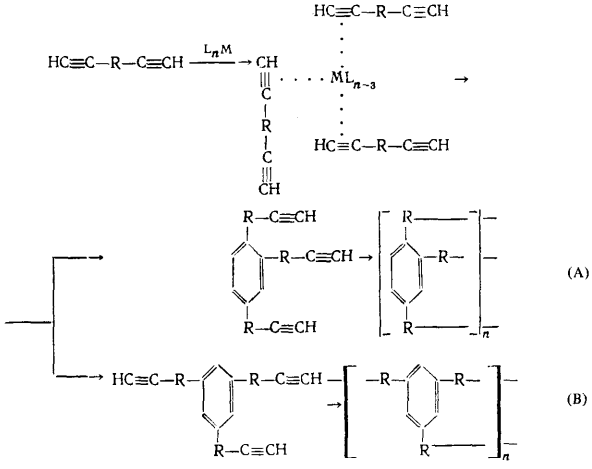
Korshak et al.[28] were the first to develop the new method for obtaining polymers of polyphenylene type from *p*-diethynylbenzene, whose polycyclotrimerisation can be represented by the scheme



The new aromatic rings formed are substituted at positions 1,2, 4 and 1,3, 5.[29,30] The proportions of the trisubstituted aromatic isomers depend on the nature of the catalytic system (mainly a metal) and on the reaction conditions.

Kinetic investigation of the polycyclotrimerisation of *p*-diethynylbenzene in the presence of trialkyl-phosphite cobalt complexes of general formula $[(AlkO)_3P]_nCoHal$ (where $n = 3$ or 4) has established[31] that the degree of conversion of the initial monomer depends not only on its initial concentration and that of the catalyst but also on the nature of the organic solvent and the duration of heating. Almost complete (97%) conversion of *p*-diethynylbenzene into a polymer can be achieved by selecting appropriate conditions by trial and error. The kinetic order with respect to *p*-diethynylbenzene is approximately first, with a rate constant of 0.01183 s^{-1}. Polycyclotrimerisation on the above catalytic complex forms strongly branched polymers containing mainly unsymmetrically trisubstituted benzene rings. This was demonstrated by nuclear magnetic resonance data for soluble specimens obtained in the initial stages at low degrees of conversion[31].

The reactions involved in the catalytic polycyclotrimerisation of diacetylenes can be represented by the general scheme[20,31]

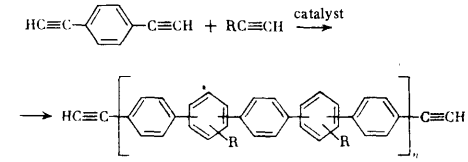


where L_nM is a catalytic complex of a metal M and a ligand L. The reaction mechanism may involve other intermediate stages, but the slowest stage is probably interaction of the intermediate complex with the third acetylenic group[20,31].

Polymers of polyphenylene type based on *p*-diethynylbenzene are yellow-brown powders. The maximum molecular weight of the soluble polyphenylenes reaches 2600. However, the reaction mixture may also contain a large quantity of alcohol-soluble oligophenylenes of molecular weight $\geqslant 350$ together with insoluble and infusible polyphenylenes, which are amorphous to X-rays, in contrast to the crystalline poly-*p*-phenylenes obtained by the oxidative dehydropolycondensation of benzene[32]. The infusible amorphous polyphenylenes from *p*-diethynylbenzene do not dissolve when heated in chlorosulphuric and concentrated sulphuric acids, an indication of their cross-linked structure. The comparatively high yield of lower oligomers at 86% conversion is attributed to relatively low reactivity of the macromolecular products (in comparison with the monomer), which may be due to steric inhibition of cyclotrimerisation in the highly branched polymer[33].

Soluble polyphenylenes are formed from *p*-diethynylbenzene in the presence of titanium tetrachloride and diethylaluminium chloride or of a nickel(II) catalyst up to 88.5% conversion of the monomer[33]. The number-average molecular weights of the polymers measured osmometrically increase slowly with conversion of the monomer, but remain fairly low (up to 1460). Complete transformation of the reaction product into a high polymer occurs at ~90% conversion, close to the point of gel formation, which corresponds to a content of 8 mass % of ethynyl groups in the polymer. The properties of the soluble oligophenylenes based on *p*-diethynylbenzene depend largely on their content of unchanged ethynyl groups, whose presence is due to the incompleteness of polycyclotrimerisation. When such oligophenylenes are heated, the ethynyl groups are involved in polymerisation and the formation of three-dimensional structures.

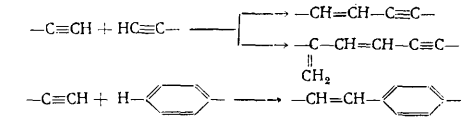
Thus the polycyclotrimerisation of *p*-diethynylbenzene yields either strongly cross-linked polyphenylenes or branched oligophenylenes of relatively low molecular weight. In order to obtain soluble oligophenylenes of higher molecular weight one active position in the newly formed benzene ring was blocked during chain growth. This was achieved by using as initial monomers various mixtures of aromatic and aliphatic mono- and di-ethynyl derivatives, whose copolycyclotrimerisation can be represented by the general scheme



where R = Ar, Alk, $CH_2:CH$, etc.

The copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene has been studied[34] in the presence of $[(C_2H_5O)_3P]_4CoBr$ as catalyst. However, when the process was conducted under conditions similar to those for the polycyclotrimerisation of the diyne, even when the initial mixture contained three moles of phenylacetylene per mole of the diyne, insoluble polyphenylenes were formed in yields up to 16%. Kinetic investigation established[34] that the rate of conversion of *p*-diethynylbenzene exceeded considerably that of phenylacetylene under the same conditions.

The polyphenylenes obtained by the polycyclotrimerisation of a mixture of *p*-diethynylbenzene and phenylacetylene were oily or solid products, whose properties were directly dependent on the reaction conditions, primarily on the molecular proportion of phenylacetylene and the initial concentrations of the acetylenes. Soluble and insoluble polyphenylenes were obtained; the infrared spectra indicated that those of greater molecular mass had lower contents of ethynyl groups relative to the aromatic portion of the polymer molecule. The maximum molecular weight of the soluble polyphenylenes was 4800. When soluble polyphenylenes containing terminal ethynyl groups were heated, they set with the formation of infusible and insoluble products, in which the process of structure formation could be represented[35]

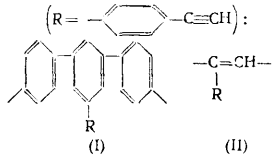


A catalytic system of the Ziegler–Natta type, comprising a trialkylaluminium and titanium(IV) chloride, is most often used for the copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene. Such a system in which the alkyl was isobutyl was employed[36] because the trimerisation of phenylacetylene in the presence of such a catalyst gave 1,3,5-triphenylbenzene in almost theoretical yield. In order to obtain soluble polyphenylenes of more regular

structure by the preferential formation of 1,3,5-substituted benzene rings, therefore, the copolycyclotrimerisation of *p*-diethynylbenzene with various quantities of phenylacetylene was conducted in solution (in heptane) at room temperature. Polymers that were completely soluble in benzene, toluene, and other organic solvents were obtained only when the molecular ratio of phenylacetylene exceeded unity[36]. Yet copolycyclotrimerisation of the components in benzene solution in the presence of the above catalyst at 60°C gave soluble and insoluble products, with the yield of insoluble polymers and the molecular weights of the soluble oligophenylenes (1170–5300) almost independent of the initial proportions of the monomers (within the range 1 : 2, 1 : 1, and 2 : 1).[37]

Infrared spectral data and kinetic investigation by gas-liquid chromatography of copolycyclotrimerisation indicated that, with the catalyst ratio Al/Ti = 0.5 at 60°C, the rate of conversion of phenylacetylene and *p*-diethynylbenzene changed as the reaction progressed. The ratio of the numbers of diyne and monoyne molecules that have reacted after 8 h at the same total concentration but different molecular concentrations of the monomers, together with the composition of the soluble copolymers determined from the intensity of the 710-cm^{-1} band characteristic of a monosubstituted benzene ring, shows that only at a molar ratio of diyne to monoyne of 2 : 1 is predominant formation of structural units of the above types (A) and (B) possible[37].

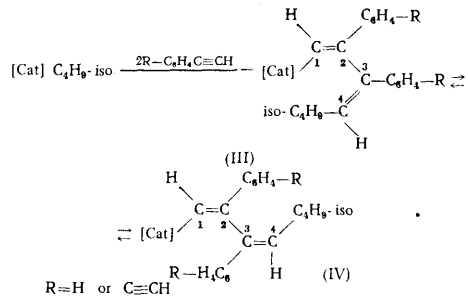
Investigation of the kinetics of the addition of ozone and the composition of the decomposition products from the ozonides indicated[37] structural non-uniformity of the soluble copolymers independently of the initial ratio of the monomers. The products of ozonolysis included benzoic and terephthalic acids. Thus the complicated mechanism of the copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene may result in copolymers containing not only phenylene segments but also anomalous units, including polyene segments. The study[38] of the influence of such anomalous units on certain properties of the copolymers formed from various ratios of the monomers in the presence of the tri-isobutylaluminium—titanium(IV) chloride catalytic system in benzene solution at 60°C revealed that increase in the proportion of the diyne in the initial mixture increased the content of triple bonds and polyene segments in the soluble oligomers. This may be due to the presence in the copolymer of the structures (I) and (II).



(I) (II)

since terephthalic acid was detected in the products of ozonolysis, whereas different acids were present in the degradation products from insoluble fractions of copolymers and homopolymers.

The formation of linear (polyene) and aromatic structures in the polymers involves cleavage of a triple bond[39], a cyclic trimer being formed by detachment of a linear trimer from a catalytic centre with ring closure[40]. This process depends not only on the nature of the acetylenic compounds and the catalytic system but also on the conditions of polycyclotrimerisation. With *trans*-cleavage of the triple bond, for example, linear polyenes are formed owing to the impossibility of *trans–cis* isomerisation with respect to the resulting double bond; with *cis*-cleavage of the triple bond, *cis-s*-cisoid (III) and *cis-s*-transoid (IV) conformations can be formed, responsible for the formation of cyclic and linear fragments respectively:



Cyclotrimerisation predominates in the case of phenylacetylene (R = H), which indicates *cis*-cleavage of the triple bond and free rotation about the $C_{(2)} - C_{(3)}$ single bond. In copolymers with *p*-diethynylbenzene (R = C⋮CH) rotation about this single bond is hindered owing to the formation of branched and cross-linked structures, which increases the probability of polyenisation. These ideas find experimental support: increasing the diyne content in the mixture impedes polycyclotrimerisation and creates conditions for the formation of polyene structures, the quantity of which is determined from the quantity of ozone added per unit weight of the copolymer.

Investigations of the structural direction of copolymerisation of these monomers on the $AlR_3-(TiCl_4)_n$ catalytic system (R = C_2H_5 or iso-C_4H_9) have also revealed[41,42] that polycyclotrimerisation is not the only process of macromolecular chain growth.

In order to formulate optimum conditions for polycyclotrimerisation to high degrees of conversion of the initial acetylenic compounds into fusible and soluble polyphenylenes of practical interest the copolycyclotrimerisation of mono- and di-acetylenic compounds was studied[43,44] in the presence of the catalytic systems

$$[(C_2H_5O)_3P]_4CoBr;\quad NiCl_2\cdot 2P(C_6H_5)_3\cdot 2NaBH_4;$$

$$Ni(CO)_2\cdot[P(OC_6H_5)_3]_2\ ;\quad Al\ (iso\text{-}C_4H_9)_3—[TiCl_4]_n.$$

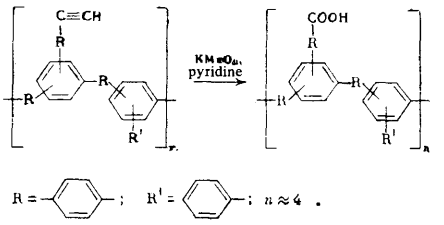
This involved preliminary preparation of complexes of the catalytic systems—the triethyl-phosphite complex of cobalt and the mixed organometallic catalyst based on triphenylphosphine, nickel chloride, and sodium tetrahydroborate—with *p*-diethynylbenzene and phenylacetylene followed by examination of their structure. In the presence of the first catalytic system above the rate of polycyclotrimerisation could be controlled by the introduction of electron-donor additives such as tertiary amines into the reaction mass or of electrophilic substituents, e.g. chlorine, bromine, etc., into the aromatic ring of the phenylacetylene. Copolycyclotrimerisation is strongly activated by electron-donor additives: the rate increases sharply, the induction period disappears, and the range of simultaneous conversion of the initial monomer mixture is enlarged.

High yields (~70%) of copolymers are obtained by copolycyclotrimerisation in the presence of the catalytic system $NiCl_2.2(C_6H_5)_3P.2NaBH_4$ under comparatively mild conditions with high rates of conversion of the initial monomers. The yield of soluble products increases considerably with increase in the phenylacetylene content of the initial mixture, and completely soluble oligophenylenes free from terminal ethynyl groups are formed when its molecular ratio to *p*-diethynylbenzene is 4 : 1. Use of a *p*-halogenophenylacetylene in copolycyclotrimerisation

enabled[43,44] the relative activities of acetylenic monomers in the reaction to be assessed and in most cases highly halogenated soluble copolymers to be synthesised.

Thus it follows from the above results that the nature of the catalytic complexes has a significant influence on the conditions of polycyclotrimerisation, on the relative reactivities of mono- and di-yne, and on the structure and properties of the resulting copolymer.

A method of oxidising toluene-soluble oligophenylenes obtained in the presence of a Ziegler–Natta type of catalyst (iso-$C_4H_9)_3Al-(TiCl_4)_n$, a mixed organometallic catalyst $NiCl_2.2(C_6H_5)_3P.2NaBG_4$, and also $(C_8H_7O_2)_2Ni.(C_6H_5)_3P$ and $[(C_2H_5O)_3P]_4CoBr$ has been devised[45,46] in order to make a comparative assessment of the efficiency and ascertain the influence of different catalytic systems on copolycyclotrimerisation, as well as to establish the structure of the polymeric products. Since multiple (double and triple) carbon–carbon bonds are readily oxidised in the presence of chromic and nitric acids or potassium permanganate, and their rupture produces organic acids or ketones[47–49], oxidation of the oligophenylenes followed the scheme



The oxidation products were pale grey powders soluble in pyridine, dioxan, dimethylformamide, and oxolan.

Properties of oxidised oligophenylenes[47–49].

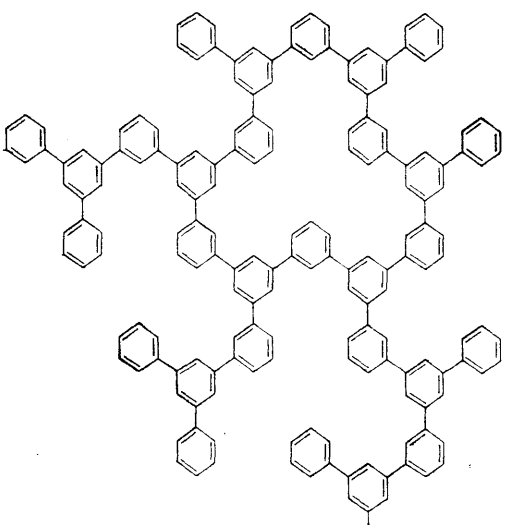
Catalytic system	Acid value, mg KOH g^{-1}	M.p., °C	Yield, %
Al (iso-$C_4H_9)_3$—$[TiCl_4]_n$	63.0	207–213	60.0
Al (iso-$C_4H_9)_3$—$[TiCl_4]_n$	75.5	250–260	60.6
$NiCl_2 \cdot 2P(C_6H_5)_3 \cdot 2NaBH_4$	71.5	130–139	34.2
Ni $(C_8H_7O_2)_2 \cdot P(C_6H_5)_3$	71.2	275–279	21.0
$[(C_2H_5O)_3P]_4CoBr$	80.0	178–193	23.6

The Table shows that the acid values and the melting points of the oxidised products depend on the conditions of formation and the structure of the initial oligophenylenes. Thus oligophenylene obtained in the presence of the sodium tetrahydroborate catalyst melted at 130–139°C after oxidation, whereas the corresponding temperatures obtained with a Ziegler–Natta type of catalyst were 250–260°C. The highest yield of oxidised product was found for a *p*-diethynylbenzene-phenylacetylene oligophenylene obtained in the presence of the Ziegler–Natta type of catalyst. From the molecular weights of the methyl ester of this copolymer (1800) and the content of methoxy-groups (6.3%) it follows that the macromolecule of the oxidised oligophenylene contains ~4 carboxy-groups. Alcohol-soluble lower oxidation products were isolated by precipitates in water; they had molecular weights of 300–450, acid values 100 to 160, and melting points 120–160°C depending on the structure of the initial oligophenylenes.

Decarboxylation of the oligophenylenecarboxylic acids at 400°C gave high yields of products having molecular weights close to those of the initial oligophenylenes (before oxidation) and with an elementary composition close to that calculated theoretically for oligophenylenes free from groups and bonds other than aromatic rings. Furthermore, acid values and infrared spectra indicated that the products contained no carboxy-groups and were almost devoid of multiple bonds, since the iodine values were close to zero. Since the initial oligophenylene, the methyl oligophenylenecarboxylate, and the product of decarboxylation of the oligophenylenecarboxylic acid had molecular weights of the same order, it was concluded[47–49] that the higher the yield of oxidised product (oligophenylenecarboxylic acid) the greater the extent of copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene, the dominant process in the presence of the Ziegler–Natta catalyst (iso-$C_4H_9)_3Al-(TiCl_4)_n$.

Synthesis of soluble branched polyphenylenes of high molecular weight by polycyclotrimerisation of a mixture of *m*-diethynylbenzene and phenylacetylene in chlorobenzene solution was accomplished[50] in the presence of a Fischer catalyst, the active principles of which are complexes $TiCl_2.(AlCl_3)_n$, where $n = 1$ or 2. Examination of the effect of the molecular ratio of the initial monomers on the properties of the products revealed that soluble polyphenylenes were obtained with up to 50% excesses of the diyne. The yield of methanol-insoluble fractions was 88%; gas chromatography revealed neither of the initial monomers in the lower fractions. The resulting polyphenylenes were cream-coloured powders soluble in chlorinated hydrocarbons and cyclic ethers. They softened at ~320°C and had number-average molecular weights up to 70 000 (measured osmometrically in chlorobenzene solution at 30°C). The ultraviolet and infrared spectra of the polymers contained absorption bands characteristic of mono-, di-, and trisubstituted aromatic rings, but none indicating terminal ethynyl groups.

Thus the resulting polymers probably had a branched structure with macrocyclic polyphenylene fragments in the chain



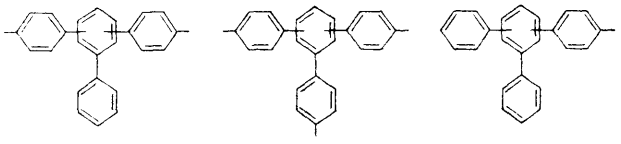
The formation of macrorings within a polymer molecule explains also the appearance of soluble polyphenylenes of high molecular weight when excess of *m*-diethynylbenzene is present (up to 1.5 moles per mole of phenylacetylene).

Soluble copolymers have been obtained[51] by heating an equimolecular mixture of phenylacetylene with a 9 : 1 mixture of *m*- and *p*-diethynylbenzenes in the presence of a catalyst $Ni(CO)_2.2(C_6H_5)_3P$ in benzene. Infrared bands characteristic of triple bonds ⋮CH and C⋮C (3300 and 2100 cm^{-1} respectively) were absent, but the appearance of an absorption band in the region of 965 cm^{-1}, typical of terminal *trans*-disubstituted double bonds, was regarded as attributable only to linear telomerisation of acetylenic compounds[52]. Solid cross-linked products separated when solutions of the copolymers were allowed to stand in the air.

Copolymers readily soluble in aromatic solvents have been obtained[51] by the copolycyclotrimerisation of the above diethynylbenzene mixture with phenylacetylene or *m*-ethynyltoluene in the presence of a $(C_2H_5)_2AlCl-(TiCl_4)_n$ catalyst (with Al : Ti = 3 : 1), which converts[53] phenylacetylene into a high (up to 80%) yield of triphenylbenzene with only slight quantities of linear products. Infrared and ^1H and ^{13}C nuclear magnetic resonance data indicate that the copolymers contain predominantly aromatic groups with very minute quantities of double and triple bonds. The reactions of these triple bonds are not those typical of terminal acetylenic compounds, since attempts to increase the molecular weight of the products by oxidative dehydropolycondensation were unsuccessful. Comparison of the n.m.r. absorption areas due to aromatic and aliphatic protons in the diethynylbenzene–*m*-ethynyltoluene copolymer indicated a ratio of mono- to di-functional initial compounds of 1.2–1.0.

Polycyclotrimerisation of diethynylbenzene with phenylacetylene or *m*-ethynyltoluene gave high yields of soluble copolymers having molecular masses of 10 000–50 000 and softening points of 200–300°C depending on the reaction conditions. Gel-permeation chromatography established that the degree of polydispersity and the molecular mass of the copolymers were almost unaffected by the initial catalyst concentration (over a fivefold range)[51]. The good solubility of the copolymers in organic solvents, the low viscosity of their solutions ($[\eta]$ = 0.089–0.288), and also the very great brittleness of films based on them (independently of molecular mass) provide convincing evidence of the branched structure of the copolymers. Furthermore, the value $\alpha \approx 0.5$ in the Mark–Houwink equation $[\eta] = KM_\omega^{\alpha}$ found experimentally also confirms a branched structure.

Because the effect of the catalyst is relatively non-specific the three possible aromatic groupings



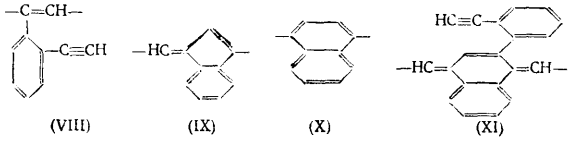
(V) (VI) (VII)

may be formed during cyclotrimerisation[51]. Group (V) arises from the interaction of one monofunctional and two difunctional molecules, and results in a linear polymer. Actually, however, groups (VI) and (VII) may also be formed, and give rise respectively to branched polymers and chain termination. Each of the groupings may in turn contain 1,2, 4- and 1,3,5-substituted aromatic rings. Two mathematical models have been suggested for theoretical calculation of the probability of formation of a particular structure at various stages of polycyclotrimerisation, and these establish foundations for conducting the process under optimum conditions and obtaining polyphenylenes having specified properties[51].

Furthermore, the statistics of branching processes based on the cascade theory has been applied[54] to the polycyclotrimerisation of *p*-diethynylbenzene and its copolycyclotrimerisation with phenylacetylene on the hypothesis of equal and constant reactivity of the ethynyl groups, with the aim of determining the degree of conversion at the point of gel formation and the mean molecular weights under random reaction conditions. The statistical estimations for the diyne indicated that the gelation point is determined by the condition $\alpha_{cr} = 0.5$: i.e. the critical degree of conversion of ethynyl groups is in this case 0.5, as for the random polycondensation of a trifunctional polymer. The values of α_{cr} calculated for the copolycyclotrimerisation increased from 0.5 to 1 with increase in the proportion of phenylacetylene in the initial mixture from 0 to 2 moles per mole of *p*-diethynylbenzene.

The possibility of controlling polycyclotrimerisation at the gel point, at which formation of a three-dimensional network begins, has been confirmed experimentally[54], and the reactivity of the ethynyl groups is shown to diminish during the reaction, probably owing to slow diffusion or steric hindrance. In discussing the properties of the resulting polyphenylenes, however, the authors unfortunately do not consider such an effect of polyenisation processes, which in some measure govern the formation of polymer molecules and their properties.

Study of the polymerisation of *o*-diethynylbenzene in the presence of various catalysts has established[55], that, in contrast to the behaviour of the *para*- and *meta*-isomers, 30–50% of the second ethynyl groups are not involved in coordination polymerisation in the presence of the catalytic systems $R_nAlCl_{3-n}-(TiCl_4)_n$ and $R_nAlCl_{3-n}.(C_5H_7O_2)_3Ti$ (where n = 1,2, or 3), 70% of these groups remain uninvolved in radical polymerisation in the presence of azoisobutyronitrile, and only one ethynyl group in the *o*-diethynylbenzene molecule reacts in cationic polymerisation in the presence of titanium tetrachloride. From these results it is assumed that polymers containing groupings of the types

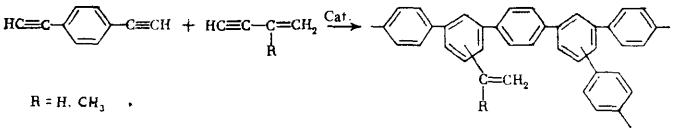


(VIII) (IX) (X) (XI)

may be formed from the *ortho*-isomer. Methyleneindane and naphthalene cyclic structures can be formed only in the presence of catalysts for coordination or radical polymerisation. However, a study of molecular models indicates[55] that formation of the six-membered cyclic structures (X) and (XI) is sterically more probable than the successive arrangement of five-membered structures (IX) in a chain, although formation of the latter is not excluded by the mechanism.

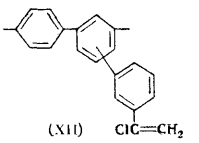
Reports have appeared[56–60] on the synthesis of branched oligophenylenes from *p*-diethynylbenzene and butadiyne or certain other monoacetylenes by polycyclotrimerisation in the presence of $(iso\text{-}C_4H_9)_3Al-(TiCl_4)_n$ (Al : Ti = 3 : 1). Polycyclotrimerisation of butadiyne or its mixture with phenylacetylene[57] gives branched oligophenylenes readily processed by hot moulding into infusible and insoluble polymeric materials distinguished by high thermal stability. This method of obtaining polyphenylenes is of definite practical interest, since butadiyne, in contrast to *p*-diethynylbenzene, is a by-product in the production of acetylene by the pyrolysis of hydrocarbon raw materials. Copolycyclotrimerisation of *p*-diethynylbenzene with hex-1-yne gives copolymers whose content of triple bonds diminishes with

increase in the proportion of the latter monomer[59]. Oligophenylenes containing free double bonds have been obtained[56] by partial or complete substitution of an alkenylacetylene—butenyne or 2-methylbutenyne—for phenylacetylene in its reaction with *p*-diethynylbenzene:



Increase in the quantity of unsaturated groups in such oligophenylenes increases their tendency to set, and plastometric tests reveal no deformation changes in hardened *p*-diethynylbenzene–2-methylbutenyne specimens even at 400°C and above, which indicates the high density of cross-linking and the enhanced thermal stability of such specimens.

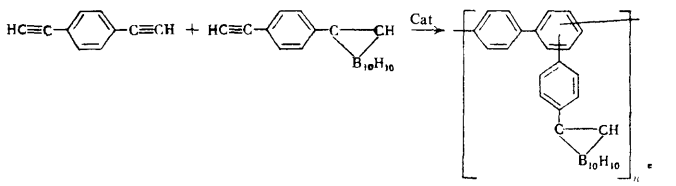
Oligophenylenes containing chlorovinyl groups



(XII)

have been obtained[60] from a mixture of *p*-diethynylbenzene, phenylacetylene, and *m*-ethynyl-1-chlorovinylbenzene. These groups not only increase the unsaturation of the resulting oligophenylenes but also confer on the polyphenylenes greater thermal stability than in the absence of this third monomer. Phenylacetylene is found to be more active than the chlorovinylethynylbenzene in polycyclotrimerisation.

Results of the model reaction of *p*-*o*'-dicarbadodecaboranylphenylacetylene in the presence of $(iso\text{-}C_4H_9)_3Al-(TiCl_4)_n$ and $NiCl_2.2(C_6H_5)_3P.2NaBH_4$, with the separation of *tris*-*p*-*o*'-dicarbaboranylphenylbenzene, suggested[58] that copolycyclotrimerisation of the former compound with *p*-diethynylbenzene could follow the scheme



Equimolecular proportions of the initial monomers gave a 75% yield of completely soluble copolymers having a boron content of 19%. They were amorphous yellow powders having M_n = 3350. With the aim of controlling the boron content in copolymers of *p*-diethynylbenzene, phenylacetylene, and *p*-*o*'-dicarbaboranylphenylacetylene in the molecular proportions 1 : 1 : 0.5 a 73% yield of a mixed copolymer having a boron content of 12% was obtained. Formation of an insoluble fraction in 20% yield was due to some inhibition of copolycyclotrimerisation of the components[58]. Thermogravimetric analysis under dynamic and isothermal conditions indicated that copolymers containing carbaboranes were highly resistant to thermal oxidation in air[58].

Polymers containing 1,2,4-substituted aromatic rings are obtained[61] by the polycyclotrimerisation of diethynyldiphenylsilane or its mixture with phenylacetylene in heptane solution in the presence of $(iso\text{-}C_4H_9)_3Al-(TiCl_4)_n$. Such polymers have smaller elastic moduli than have polyphenylenes obtained from *p*-diethynylbenzene. This is attributed to greater elasticity of the "hinge" bond in the silicon-containing polymer.

In conclusion it must be noted that a distinguishing feature of the polycyclotrimerisation of acetylenic compounds is the formation mainly of trisubstituted aromatic rings in the polymer structure[3]. The rigidity of a polymer molecule increases with the content of aromatic groups, while the polymer as a whole is characterised by high heat resistance and thermal stability[4,5]. Therefore polyphenylenes obtained by the copolycyclotrimerisation of diynes with monoynes are of definite practical interest, since they can readily be processed by the usual methods of chemical forming into articles that withstand high temperatures for a long time[30,36,51].

III. POLYCYCLOTRIMERISATION OF MONOMERS WITH MULTIPLE CARBON–NITROGEN BONDS

The polycyclotrimerisation of several compounds containing multiple carbon–nitrogen bonds was already known in the nineteenth century, but most research in this field has been undertaken during recent years. At the present time a number of cyanogen compounds—such as hydrocyanic acid, cyanogen chloride, cyanamide, acetone cyanohydrin, β-hydroxypropionitrile, acrylonitrile, etc.—are large-tonnage industrial products. Several 1,3,5-triazines (cyanuryl chloride, cyanuric acid, melamine, and their derivatives), obtained by the cyclotrimerisation and cyclocondensation of appropriate compounds, are also produced industrially on a large scale.

Research on the polycyclotrimerisation of monomers containing multiple carbon-nitrogen bonds has been widely developed only during the past decade in connection with the need for highly heat-resistant and thermostable polymers and composition materials for various branches of modern technology, especially for air and space travel. As already noted above, this method has several advantages over well known syntheses of thermostable polymers and is distinguished by the simplicity of its technical organisation, the availability of the starting materials, the absence of separation of secondary products, etc. A considerable number of publications have now appeared on the cyclotrimerisation and polycyclotrimerisation of monomers containing multiple carbon-nitrogen bonds, the synthesis and the properties of the polymers, the laws of their formation, etc.

We do not intend to discuss in detail all aspects of the problem, since several reviews have already been published in this field during recent years[3,4,7,62–66]. We shall consider recent studies of the polycyclotrimerisation of monomers with cleavage of multiple carbon–nitrogen bonds, e.g. in aliphatic, aromatic, and hetero-organic nitriles, cyanates, cyanamides, etc. Attention will be paid mainly to work on the mechanism, kinetics, and thermodynamics of polycyclotrimerisation, gel formation, the molecular weight characteristics of the polymers, the influence of the structure of the monomers on the properties of the polymers, and specific features of this synthesis of cross-linked polymers.

During recent years Korshak[7,67] has developed the concept of the heterounit character of polymers consequent on several secondary processes accompanying the main polymerisation reaction. Such structural "defectiveness" of a particular polymer leads in most cases to diminished heat resistance, thermal stability, physicomechanical indices, etc. For example, the polycyclotrimerisation of isocyanates, nitriles, and other monomers is accompanied by many secondary reactions (chain polymerisation,

dimerisation, etc.)[3,4,7,67–79]. The production of polymers of almost perfect structure is therefore an urgent problem, whose solution will improve considerably many characteristics of the polymers and may lead to materials having qualitatively novel properties.

Recent papers by Korshak and his coworkers have shown that cyanates and cyanamides are potentially the most promising and convenient compounds for studying this new field in polymer chemistry[62,64,65]. These monomers are more reactive than nitriles, which makes them convenient for investigating the laws of polycyclotrimerisation. The cyclotrimerisation of cyanates and cyanamides, in contrast to that of isocyanates, is uncomplicated by dimerisation, carbodi-imidisation, or linear polymerisation, and these compounds are considerably less subject to hydrolysis of functional groups and are stable on storage. Furthermore, cyanates and cyanamides are non-toxic, and are less volatile than isocyanates [64,65]. They can be prepared simply, in high yields from readily available starting materials[64,66]. Their great synthetic possibilities have permitted the establishment of various systematic series of initial monomers and oligomers, detailed study of the influence of their structure on the properties of the resulting polymers, and formulation of principles governing the directed synthesis of networks having specified properties[62,64,65].

1. Laws of Polycyclotrimerisation

Research on the kinetics and mechanism of the cyclotrimerisation of nitriles has been discussed in detail in several reviews[3,4,62–65], and therefore will not be considered here.

A series of papers of Korshak et al. [3,4,80–90] has been devoted to a detailed investigation of the kinetics and the mechanism of the cyclotrimerisation and polycyclotrimerisation of aryl cyanates. Since the polycyclotrimerisation of arylene dicyanates yields insoluble, infusible, highly cross-linked polymers, it is more convenient to use monofunctional cyanic esters for investigation of kinetics, heat of reaction, and also the effect of the structure of cyanic esters on reactivity. The cyclotrimerisation of phenyl cyanate into triphenyl cyanurate — a reaction that models the formation of a polymer by polycyclotrimerisation and is not complicated by such processes as gel formation, etc. — was studied first. The reaction was conducted in ditolylmethane solution in the presence of chromium acetylacetonate $(acac)_3Cr$, one of the most active catalysts for this process. The rate of cyclotrimerisation was measured by means of a double calorimeter from the quantity of heat evolved in a certain time. The reaction was found to be autocatalytic[81–90]. The heat of cyclotrimerisation of phenyl cyanate is -27.9 ± 1.4 kcal mole^{-1}. The energy of stabilisation of the 1,3,5-triazine ring has also been estimated (as 26 kcal mole^{-1}); this ring is stabilised both by delocalisation of electrons with formation of a system analogous to the π system of the benzene ring and also by partial polarisation of a cyclic nitrogen–carbon bond[81].

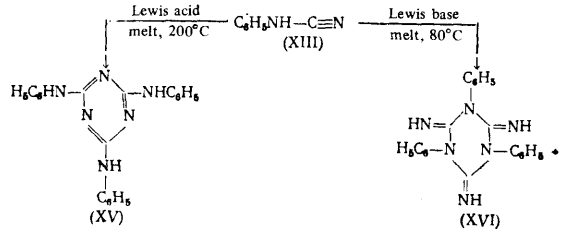
The kinetics of the conversion of various substituted aryl cyanates have been studied and the enthalpies measured to ascertain the effect of the structure of cyanic esters on their reactivity and the heat of cyclotrimerisation[89]. The nature of substituents has a significant influence on the rate. Thus electron-donor substituents (*p*-methoxyl, *p*-methyl) lower the rate of cyclotrimerisation, whereas electron-accepting substituents (*p*-chloro) increase it in comparison with that of unsubstituted phenyl cyanate. The maximum rate, the time of its achievement, and the heat of reaction are linear functions of the σ constants of the substituents[89].

Direct calorimetry has been used[83–86,88,90], under conditions analogous to those of the model reactions, to make a more thorough kinetic study and measure the heat of the polycyclotrimerisation of di-2-*p*-cyanatophenylpropane. The kinetic features are mainly the same as in the cyclotrimerisation of phenyl cyanates. The mean heat of polycyclotrimerisation of the dicyanate is $\Delta H = -56.8$ kcal mole^{-1}, i.e. 28.4 kcal mole^{-1} per N:C.O group. The close agreement between this value and the above heat of cyclotrimerisation of phenyl cyanate (−27.9) confirms the great selectivity of the polycyclotrimerisation of arylene dicyanates[83,84].

The rate of polycyclotrimerisation of di-2-*p*-cyanatophenylpropane, the heat of reaction, and also the effective activation energy depend on the nature of the solvent[88]. The solvents used can be arranged in the sequence ditolylmethane > nitrobenzene > anisole > diglyme in which the rate falls. Both physical and specific solvation of the arylene dicyanate by solvent molecules are responsible for the decreased rate and heat of polycyclotrimerisation[88]. Bonetskaya et al. [83,85,86] have found that the presence of water in the system has an appreciable effect on the rate. Gas–liquid chromatography reveals traces of pentane-2,4-dione after the reaction mass has been thermostatted at 140°C. The reaction velocity is increased by the addition of water, but diminished by that of the pentanedione. These results suggest[86,90] that an active form of the catalyst is formed by the action of water, and is present in equilibrium with the main form.

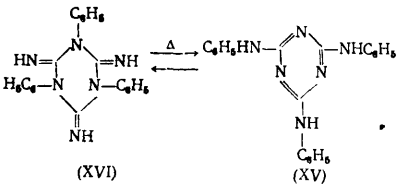
The kinetic features of the polycyclotrimerisation of arylene dicyanates established in the above studies reduce essentially to the following points. The process has a clearly defined autocatalytic character. Independently of the concentrations of catalyst and monomer, the maximum rate is observed at a definite extent of conversion (~40%) of the dicyanate. The maximum rate is proportional to the square root of the product of the concentrations of the catalyst and water, and varies linearly with the concentration of the arylene dicyanate. Addition of small quantities of pentane-2,4-dione in addition to the chromium acetylacetonate catalyst decreases the maximum rate, while the time of achievement of this maximum is sharply increased. In the absence of a catalyst additions of the final reaction products (triphenyl cyanurate or a polymer) do not catalyse the reaction[81,83–86,90].

Korshak et al. have made a series of studies[91–97] of the polycyclotrimerisation of cyanamides, another type of hetero-substituted nitriles. Phenylcyanamide (XIII) and *N*-ethylphenylcyanamide (XIV) were first chosen as model compounds. Either normal triphenylmelamine (XV) or triphenylisomelamine (XVI) could be formed depending on the conditions of cyclotrimerisation[91,92,94]:



Thus the cyclotrimerisation of (XIII) in the melt under mild conditions (20–80°C) gives (XVI), whereas at 200°C

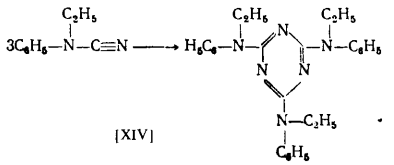
the main product is (XV). Hydrolysis of the isomeric products (XVI) and (XV) gave high yields respectively of triphenyl isocyanurate and cyanuric acid[91,92,94]. Study of the effect of temperature on the isomers showed that structure (XV) remains unchanged until it decomposes (above 400°C), whereas (XVI) isomerises into (XV) at temperatures above its melting point (185°C)[91,94]:



(XVI) (XV)

Isomerisation of (XVI) into (XV) takes place at considerably lower temperatures in solution. The normal melamine structure is more stable than the isomelamine structure at high temperatures, so that it is of greater interest for the development of thermostable polymers[91]. Korshak et al.[91,92,95,96] have investigated the action of various catalysts with the aim of directing the cyclotrimerisation of *N*-monosubstituted cyanamides to give a definite isomeric structure. They find that the formation of triphenylmelamine (XV) is favoured by catalysts such as Lewis acids (metal chlorides), but that of triphenylisomelamine (XVI) by Lewis bases.

To ascertain the effect of a substituent in the cyanamide group on the reactivity of an arylcyanamide and on the structure of the products the same workers have studied[93,94,96,97] the cyclotrimerisation of *N*-ethylphenylcyanamide (XIV)



[XIV]

The presence of the aliphatic substituent α to the nitrile group diminishes the reactivity of the cyanamide group, so that the process occurs only in the presence of such catalysts as Lewis acids. A substituted melamine of normal structure is formed: the iso-structure was not detected among the reaction products[94]. The above features of *N*-mono- and *NN*-di-substituted cyanamides and of the products of their cyclotrimerisation must be taken into account in preparing polymers from cyanamides and examining their properties.

Korshak et al.[93,94] have studied the polycyclotrimerisation of primary and secondary *N*-substituted biscyanamides. The highly reactive di-*p*-cyanamidophenylmethane begins to polymerise below its melting point of 162°C. Heating at 100°C for 2 h leads to 43% conversion. The rate of polycyclotrimerisation increases sharply at temperatures above the melting point, and at 180°C, for example, conversion reaches 87% after 30 min. As in the case of the model compound phenylcyanamide, two isomeric polymelamine structures can be formed depending on the temperature of polycyclotrimerisation of the biscyanamide: at 100 and 140°C, i.e. at temperatures below the melting point of di-*p*-cyanamidophenylmethane, the process results in formation of a polymer predominantly of isomelamine structure; at 180°C and above, i.e. above the melting point of the monomer, the main product is a polymer having the normal melamine structure[94].

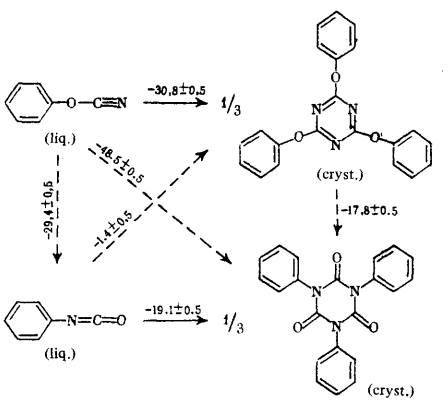
Di-*p*-*N*-methyl(and ethyl)cyanamidophenylmethane have been used as examples for kinetic study of the polycyclotrimerisation of secondary *N*-substituted cyanamides. As with the model compound (*N*-ethyl-*N*-phenylcyanamide) the presence of aliphatic substituents α to the nitrile group diminishes the reactivity of the cyanamide group in comparison with primary *N*-substituted cyanamides. Such compounds undergo polycyclotrimerisation in the presence of cationic catalysts such as Lewis acids, but hardly at all in the absence of catalysts under the same temperature conditions. An isomelamine structure was not detected[94] among the products of the polycyclotrimerisation of secondary *N*-substituted biscyanamides.

2. Thermodynamic Parameters of Cyclotrimerisation and Polycyclotrimerisation

Study of the thermodynamic parameters helps to elucidate the conditions under which polycyclotrimerisation is possible and is reversible, and will give information on the temperature range of thermodynamic stability, structural features of the resulting polymers, the relative stability of isomeric compounds, the possibility of their isomerisation, and other important aspects of the process.

Thermodynamic characteristics of the polycyclotrimerisation of dicyanates have been studied in greatest detail on di-2-*p*-cyanatophenylpropane[98]. Measurements have been made on the temperature dependence of the heat capacity of the polymer and of the initial dicyanate, as well as the enthalpies of combustion of these compounds. Calculations of enthalpy, entropy, and Gibbs free energy have been made for polycyclotrimerisation of the dicyanate into a regularly cross-linked amorphous polymer. Within the limits of experimental error the enthalpy of polymerisation $-\Delta H_{pol}$ found at 420 K coincides with the value determined by direct calorimetry (respectively 53.2 and 56.8 kcal mole^{-1}), which yet again confirms the unidirectional character of the polycyclotrimerisation of arylene dicyanates[98].

Great interest attaches to comparative estimates of the thermodynamic parameters of the cyclotrimerisation and polycyclotrimerisation of isomeric esters of cyanic acid—cyanates and isocyanates — into corresponding isomeric derivatives of cyanuric acid[99]. Because of the complexity of the investigation of cross-linked systems and the occurrence of numerous secondary processes accompanying the polycyclotrimerisation of di-isocyanates it is more convenient to examine model compounds (phenyl cyanate and isocyanate) and their trimers (triphenyl cyanurate and isocyanurate). Enthalpies of combustion of these compounds have been determined[99], and enthalpies calculated for cyclotrimerisation



and the hypothetical reactions indicated by the broken

arrows. Here the arrows indicate the directions of exothermic reactions and the numerals thereon their enthalpies (in kcal mole^{-1}) for the given physical states. Inspection of the values for the hypothetical isomerisations shows that the iso-form is considerably more stable than the normal form in both monomers and trimers. The validity of this conclusion, based on calculated values, is confirmed by published information on the isomerisation of aliphatic cyanates and alkyl cyanurates into high yields of the corresponding isocyanates and alkyl isocyanurates[64,73,100]. Despite the greater thermodynamic stability of the iso-form of the initial compounds and trimers, however, aromatic cyanates and cyanurates do not isomerise, and conditions have not yet been found which would permit such reactions[64,73,100].

A comparative thermodynamic study has been made not only on model compounds but also on di-isocyanates isomeric with arylene dicyanates[99]. The enthalpy of polycyclotrimerisation of di-*p*-isocyanatophenylmethane (-24 kcal mole^{-1}) was rather more than half the value for the dicyanate. The decrease in entropy accompanying polymerisation both of the dicyanate and of the di-isocyanate is ~36 e.u., exceeding by about 30% the value of linear polymerisation. This is a feature of polycyclotrimerisation resulting in the formation of regularly cross-linked polymers[99].

For the polycyclotrimerisation of di-2-cyanatophenylpropane over the range 100–420 K both ΔH_{pol}^0 and ΔS_{pol}^0 are negative[98]. The upper temperature limit to polymerisation of this dicyanate is 1480 K, much higher than the temperatures at which thermal decomposition of monomer and polymer begins. (Below 1480 K there is no thermodynamic hindrance to conversion of monomer into polymer, but above this temperature formation of the polymer is impossible). The absolute values of the Gibbs free energy show that the polycyclotrimerisation equilibrium for dicyanate and di-isocyanate ($-\Delta G_{pol}^0$ respectively 40.3 and 19.1 kcal mole^{-1}) is almost completely displaced towards formation of the polymer[98,99].

3. Gel Formation and Molecular Weight Characteristics in Polycyclotrimerisation

The investigation of gel formation and molecular-weight characteristics is a key to understanding the formation of three-dimensional structures. Knowledge of these processes will in turn enable the direction of the reaction to be controlled both in the initial stage of oligomerisation and following the gel point, and also polymers to be produced having a definite topological structure and thus their physicochemical and thermal properties to be influenced. Polycyclotrimerisation is a fundamentally new method for synthesising three-dimensional polymers, which enables networks of regular chemical structure to be built with segments of strictly specified size M_c between cross-links. Such systems are ideal models for experimental investigation of gel formation.

Korshak et al.[101–103] have used aromatic dicyanates and the isomeric di-isocyanates to make a detailed investigation of the influence on gel formation of such factors as method of synthesis, nature of solvent, catalyst, and monomer, and also monomer and catalyst concentrations. Di-2-*p*-cyanatophenylpropane and di-*p*-isocyanatophenylmethane were used as initial monomers. The gel point and the dependence of yield of gel on degree of conversion are governed by the method of synthesis and the solvent employed. The type of catalyst affects these parameters only in certain solvents[101].

The influence of monomer concentration on the character of gel formation depends on the nature of the solvent. With decrease in concentration in a "good" solvent (nitrobenzene, chlorobenzene) the conversion at the gel point increases, whereas in a "bad" solvent (ditolylmethane) the dependence is "anomalous", i.e. the conversion at the gel point diminishes[101].

No appreciable effect of temperature on gel formation was observed. On polycyclotrimerisation in the mass of either of the above monomers the main parameters of gel formation were unaffected by nature or concentration of the catalyst[102].

The close agreement of several of the main rules of gel formation in the polycyclotrimerisation of dicyanates and of di-isocyanates, i.e. of different classes of monomers, together with investigation of the molecular weight characteristics during the reaction up to the gel point and the sol fraction after this point, has enabled general ideas to be formulated on the construction of a topological gel structure in this method of synthesising cross-linked polymers[102,103]. Comparison of the experimental results [102] with the theory of gel formation developed for polycyclotrimerisation reveals close agreement in several cases. Differences existing between calculated and experimental values are explained by the fact that the theory ignores the macrocyclisation resulting from the considerable branching of the macromolecules[102,103].

Traditional methods of synthesising cross-linked polymers from monomers, oligomers, or polyfunctional polymers are complicated by such factors as differences in reactivity between functional groups not leading to branching, a difficultly controllable distribution among molecular weights and types of functionality for initial oligomers and polymers, and many others. All this makes it difficult to synthesise cross-linked polymers having a chemically regular structure. Polycyclotrimerisation eliminates most of these disadvantages and enables polymers to be obtained that are regularly cross-linked at a molecular level. In this method of synthesis the entry of each functional group into reaction is accompanied by branching of the macromolecule, except for the "loss" of functional groups on macrocyclisation.

The detailed investigation of gel formation and molecular weight characteristics made by Korshak and his coworkers[101–103] has shown that macrocyclisation can be controlled by varying the reaction conditions. This in turn affects the topological structure of the resulting polymers. The possibility of acting at a higher (than molecular) level of structural organisation of the networks opens up great prospects for controlling the physical properties of cross-linked polymers by changing their topology.

4. Structure and Properties of Polymers obtained by Polycyclotrimerisation

The main types of monomers that have been widely investigated in polycyclotrimerisation are isocyanates, nitriles, cyanates, and cyanamides. Many papers have been published on the cyclotrimerisation and polycyclotrimerisation of isocyanates, and the results have been summarised in several exhaustive reviews[3,4,68–75,77–79]. Discussion of the polycyclotrimerisation of monomers of this type lies outside the scope of the present Review; we note merely that several interesting studies have recently appeared on

the mechanism of the cyclotrimerisation of isocyanates[104,105]. However, polycyclotrimerisation of isocyanates with formation of cross-linked structures has been little studied, and published views on its mechanism are often contradictory[3,4,68–75,77–79,106–111].

Most of the information on polymers based on isocyanates comes from the patent literature, from which in most cases it is difficult to assess the structure of the polymers or the presence of secondary structures. Among the known groups of compounds that form cyclotrimers isocyanates are most likely to undergo various secondary reactions—dimerisation, carbodi-imidisation, linear polymerisation, chain termination by hydrolysis of isocyanato-groups, etc.—accompanying cyclotrimerisation. The occurrence of these numerous secondary processes, which are extremely difficult to eliminate, is the main hindrance to investigation of the polycyclotrimerisation of isocyanates and a correct interpretation of the results in relation to the reaction mechanism and the structure of the resulting cross-linked polymers.

Nitriles are usually unreactive in comparison with isocyanates, and their polycyclotrimerisation requires severe conditions (high temperatures, pressures, catalyst contents, etc.), which hinders their processing into articles. A considerable content of catalysts (usually highly active compounds) in the cross-linked polymer also affects adversely the thermal stability and other properties of materials obtained from such polymers[3,4,7,62,63,65]. Furthermore, the cyclotrimerisation of nitriles may be accompanied by several secondary processes—linear polymerisation of cyano-groups with formation of azomethine structures, chain termination by various reactions of nitrile groups in the presence of a high content of catalytic systems, formation of cyclic products by aliphatic nitriles, etc.—especially under severe conditions. The presence in such polymers of various "defect" structures makes difficult the formation of a chemically regular network, which in turn diminishes their thermal and physicochemical characteristics[3,4,7,62,63,65]. In the Reviewers' opinion necessary conditions for overcoming these disadvanatages of the synthesis of cross-linked polymers by the polycyclotrimerisation of nitriles are— the discovery of highly active catalysts for polycyclotrimerisation, development of convenient and cheap methods for obtaining the initial monomers, and also synthesis of nitriles containing electron-accepting groups to strengthen polarisation of the N⋮C bonds.

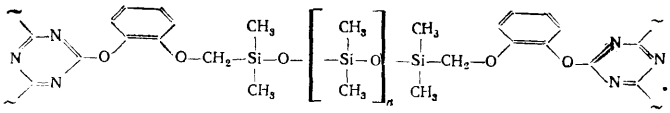
Korshak and his coworkers[3,4,62,64,65,80–99,101–103] have shown that, in contrast to isocyanates and nitriles, cyanates and cyanamides undergo highly selective polycyclotrimerisation under certain conditions with almost quantitative conversion of functional groups. The resulting polycyanurates and polymelamines are highly cross-linked heterochain polymers with 1,3, 5-triazine rings as branch points separated by segments of aromatic and heterorganic diols, glycols, and diamines[80–99,101–103,112–152]. Such polymers, especially those having highly cross-linked aromatic structures, were not known previously. In contrast to randomly cross-linked systems, polymers having a chemically regular network should exhibit a qualitative change in several properties of cross-linked polymers. Thus polycyanurates surpass in heat resistance and thermal stability the similarly constructed polyisocyanurates obtained from di-isocyanates, although the study of model compounds shows that the isocyanurate ring is thermally more stable than the cyanurate ring[73,74,113,118,120]. The presence of numerous "defect" structures—urea groups, linear structures, dimers, etc.—probably has a considerable influence on the thermal stability of polymers obtained by the cyclotrimerisation of di-isocyanates. In contrast to all known highly cross-linked aromatic polymers block polycyanurate specimens have abnormally high specific impact resistance (up to 30 kgf cm^{-1} cm^{-2}) and are distinguished by good physicochemical indices both at room temperature and at high temperatures[112,113,122].

In order to ascertain the causes of the unusual mechanical properties of polycyanurates electron microscopy has been used to monitor the formation of a supermolecular structure at various stages of synthesis[123]. The product of the early stages of polycyclotrimerisation has a globular structure, and then aggregation of the globules is observed, leading in the final stage (on 98% conversion of cyanato-groups) to fibrillar organisations. Parallel with the investigation of the super molecular structure of polycyanurates a study was made of the relaxation properties of the solid networks formed at various stages of conversion of the cyanato-groups of the initial monomer (di-2-*p*-cyanatophenylpropane). With increase in the degree of conversion the relaxation curves first moved to higher stresses, but after ~90% conversion of the monomer they then began to move into the region of lower stresses. The results indicate that, as the polycyclotrimerisation of arylene dicyanates progresses, and hence the network becomes more regular, the character of the supermolecular structure changes from the simplest globular form to fibrillar structures, which in turn leads to a regular variation in the mechanical properties of the cross-linked systems, to diminished brittleness and enhanced elasticity[123]. Perhaps obtaining in the usual thermosetting systems a regular network free from defects might also yield polymeric materials of enhanced elasticity and impact resistance.

Another interesting feature of, regular highly cross-linked polymers obtained by the polycyclotrimerisation of monomers containing multiple carbon-nitrogen bonds is their ability to crystallise. Although crystalline cross-linked polymers had been known[153–158], they contained as segments M_S between cross-links flexible aliphatic and siloxane fragments with $M_S \geqslant 2000$, and their crystalline structure was completely analogous to that of the initial oligomers. Korshak et al.[124] have been the first to obtain highly cross-linked rigid-chain polymers (for a polycyanurate based on *p*-phenylene dicyanate $M_S = 108$) of completely different structure from that of the original crystalline monomer. A tendency to crystallise has been observed in several polycyanurates and polymelamines obtained from various aromatic dicyanates and biscyanamides[93,94,112,113]. The ability of polycyanurates to crystallise, like many other usual properties of these polymers, is a consequence of their regular structure resulting from highly selective cyclotrimerisation of the cyanato-groups in the initial monomers and almost complete quantitative polycyclotrimerisation of the dicyanates.

In order to assess the density of packing of macromolecules in cross-linked polymers and establish the influence of the chemical structure of the initial monomers Korshak et al.[122] have been the first to calculate packing coefficients for such systems. Values for cross-linked polymers of diverse structure are found to lie within the narrow limits 0.673–0.698, close to the mean value 0.681 for linear polymers[159]. An exception is provided by polycyanurates containing dimethylsiloxane segments of various lengths

between junction points of the network



These polymers have abnormally low packing coefficients K, which decrease as M_S increases, from 0.651 to 0.587 with increase in n from 0 to 100.[131,152] Special determination on these systems showed zero porosity, so that these abnormally low packing coefficients can be attributed to loose packing of the macromolecules of the organosilicon polycyanurates[131,152].

Control of the chemical nature and length of the network segments has permitted monitoring of the influence of these parameters on the properties of cross-linked polymers obtained by the polycyclotrimerisation of monomers containing multiple carbon–nitrogen bonds, which in turn has led to directed improvement of the heat resistance, thermal stability, and physicomechanical indices of polymeric materials.

Besides aromatic polycyanurates and polymelamines, polymers of this type have been synthesised from organofluorine, organoboron, and organosilicon monomers. The presence of perfluorinated segments between cross-links in the structure of polycyanurates leads to glass points from −40 to +350°C.[116,134] Such polymers can be used as thermostable films, adhesives, and elastomers possessing improved flame resistance[134].

Polymers containing carbaborane fragments possess several unique properties, among which the most interesting is the high carbon residue at high temperatures (up to 1000°C), often with retention of definite strength properties[115,135,137,141,142,149]. Korshak, Andrianov, et al. have prepared organosilicon polycyanurates[127-131,145-147,152], which have glass points from −120 to +180°C depending on the length of the siloxane chain between the cross-links. These polymers possess high thermal stability with a wide temperature range of the hyperelastic state, from −120 to +340°C, i.e. up to the temperatures at which they begin to degrade[145-147,152].

The influence of the length of network segments on the properties of polycyanurates and polymelamines has been investigated also on the products of the polycyclotrimerisation of oligoarylates, oligo(arylene sulphones), and oligoamides with terminal cyanato- or cyanamido-groups[64,65].

A method based on the statistical theory of hyperelasticity has been used to examine the main parameters of the network structure of polymers obtained from oligodicyanates[131,152]. It involves measuring the stress relaxation at constant deformation on uniaxial extension of the polycyanurate films. The experimental number-average molecular masses and concentrations of active chains in unit volume of the cross-linked polymers are similar in magnitude to those calculated theoretically, which is evidence of selectivity of polycyclotrimerisation and quantitative conversion of the cyanato-groups of the oligodicyanates[131,152].

The size of the cross-linked segment influences also several other physicomechanical indices of the polycyanurates. Thus polymers containing dimethylsiloxane segments show a sharp increase in tensile strength and higher elastic moduli with increase in the frequency of cross-linking[131,152]. Enhancement of tensile, bending, and compressive strengths with increase in network frequency has been found also with polycyanurates containing aromatic oligoester segments[152].

In addition to the wide modification of properties of polycyanurates and polymelamines by the use of particular initial dicyanates and biscyanamides, several studies have shown that physicomechanical and thermal properties can be varied by synthesising copolymers of dicyanates and biscyanamides with monocyanates, nitriles, cyanamides, isocyanates, and acid anhydrides[64,65,94,117,125,126,133,134,138,151,152].

The very promising outlook for polycyclotrimerisation as a method for synthesising cross-linked systems having a regular chemical structure has been demonstrated by the combined study by Korshak and his collarborators[80-99, 101-103,112-152] of the synthesis of monomers and polymers and the physical properties of cross-linked systems obtained from monomers containing multiple carbon-nitrogen bonds. Thus several polycyanurates formed from aromatic and hetero-organic dicyanates possess high physicochemical indices, considerably surpassing in this respect most known highly cross-linked rigid-chain polymers[64,112,113,122]. The majority of cross-linked polymers obtained are characterised by high heat resistance and thermal stability: they begin to lose mass at about 400°C or above; and highly cross-linked systems do not soften right up to their decomposition temperature[64,65,93,94,112,113,119,122].

From the above account it may be concluded that polymers based on cyanates and cyanamides are of great practical interest. All the reagents required to prepare the initial monomers (phenolic diols, diamines, cyanogen chloride, triethylamine, acetone) are multitonnage industrial products. The monomers are obtained at temperatures of 0–20°C by technically simple processes. The yields of cyanates and cyanamides are close to theoretical. The products possess great stability, can be stored at room temperature for a long time, and are nontoxic. Their processing into goods via an oligomerisation stage is accomplished by gradually heating the initial monomers, does not require special equipment, and can be undertaken directly at the site at which the goods are obtained from the polymers[64,65]. Materials based on polycyanurates and polymelamines (adhesives, coatings, filled plastics, insulating compounds, etc.) possess excellent physicochemical properties and thermal stability[64,65,93,94,112,113,122,132-152].

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Advances in the Production of Thermostable Antifrication Plastics

I.A.Gribova and O.V.Vinogradova

Methods of producing self-lubricating antifriction plastics are examined. Filling with a solid lubricant a polymeric binder that does not possess a low coefficient of friction when unfilled is a promising development. The principal physicochemical requirements to be met by a polymer to be used as a binder are formulated. Possible chemical changes undergone by the polymeric binder and the filler during friction are discussed. Published information on the effect of the chemical nature of the polymeric binder on the properties of antifriction materials is summarised. The Review concludes with 211 references.

CONTENTS

I. Introduction 94
II. Production of thermostable self-lubricating antifriction plastics 94
III. Chemical reactions of polymeric binder and of filler during friction 99
IV. Properties of thermostable antifriction plastics 100

I. INTRODUCTION

Many polymeric antifriction materials are known that can be used in friction units. Polymeric materials are far more effective in their antifriction properties than are antifriction alloys[1-6], graphitic and oil-filled bronzes[7]. Polymeric antifriction materials are distinguished by the ease of production of articles, low specific gravity, good antifriction properties, and the possibility of modifying the properties of the polymers by simple technical operations. They can be applied to friction units in various ways—by coating a metal surface with a thin layer of the polymer, making parts from blocks of the polymer with and without fillers, or impregnating a porous metal base with the polymer[8].

Materials possessing antifriction properties now face increasingly severe demands—high heat resistance and thermal stability, vibration strength, radiation resistance, good machinability. They should ensure the functioning of friction units under extreme conditions—high and low temperatures (from +500 to −200°C), corrosive media, high vacua, great speeds, and high unit loads. The use of liquid lubricants under these conditions is ineffective.

The attention of investigators has therefore been attracted to multicomponent materials, in which the functions of structural material and lubricant are combined. The production of such materials having specified properties is an extremely complicated task. Account must be taken of the nature of the polymeric binder, the properties, composition, and quantity of fillers added, and also the chemical and physicochemical processes involved in interaction between polymer and fillers[9-15].

Numerous investigations have been made on the friction of solids, including polymeric antifriction materials, which have been summarised in monographs[16-28], proceedings of conferences[29-31], reviews[32-36], and individual papers[37-42]. However, this research has been concerned with problems of the mechanics, technology, and physical chemistry of filled systems. Considerably less attention has been paid to chemical aspects of the production of antifriction plastics.

The present Review examines the influence of the chemical nature of the polymeric binder on the properties of antifriction materials, and also on the chemical and physicochemical changes undergone by the components during friction.

II. PRODUCTION OF THERMOSTABLE SELF-LUBRICATING ANTIFRICTION PLASTICS

Self-lubricating antifriction plastics can be obtained in two fundamentally different ways. A method widely discussed in the literature is to produce materials based on polytetrafluoroethylene[21,43-52], Thiokols[53,54], and other polymers possessing good lubricating properties and low coefficients of friction (~0.1). In this case the lubricating principle is the polymer itself, while the introduction of fillers merely improves its physicomechanical properties—by enhancing thermal conductivity, wear resistance, hardness, strength, and heat resistance, and by diminishing cold flow.

The second method is to obtain materials based on polymers having a comparatively high coefficient of friction (0.1–0.5). Such polymers include polyhydrocarbons, halogenated polyhydrocarbons, polyamides, polyesters, polyurethanes, phenolic resins, etc. Solid or liquid lubricants are generally included in the composition of such polymers for use in dry friction units. This process was made possible by research on highly filled polymers undertaken during 1949–1950 by Rebinder and his school[55,56]. This second method is most promising, since it opens up wide opportunities of purposeful searching for binders among a large number of known and new polymers.

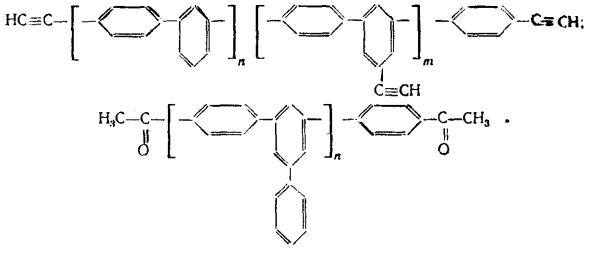
In order to solve the problem of producing the heat-resistant and thermostable self-lubricating antifriction plastics required by modern technology a broad research programme on filled antifriction polymer systems has been followed under the direction of V. V. Korshak in the Institute of Hetero-organic Compounds of the USSR Academy of Sciences. These investigations included study of the influence of the chemical structure of the polymers, their physical structure, and also the chemical nature of the filler and the strength of polymer–filler bonding on the properties of the antifriction plastics, study of the behaviour of filled systems during friction at high temperatures, as well as aspects of structure formation and the synthesis of network polymers in the presence of fillers under processing conditions, and study of the properties and the stabilisation of filled polymers.

Advances made in the synthesis of thermostable polymers, establishment of the relation between the chemical

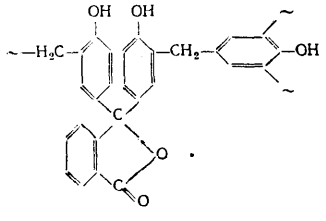
structure of polymers and their properties, and the hetero-unit character of polymers have offered wide opportunities for the production of antifriction plastics[57–59]. Both thermoplastic and thermosetting polymers of diverse chemical structure have been used as binders in the development of self-lubricating antifriction plastics. Choice has concentrated mainly on members (see List) of new classes of thermostable rigid-chain organic and hetero-organic polymers containing rings in the chain, bulky side-groups, hetero-groups, cross-links (such polymers include polyphenylenes, phenolphthalein–phenol–formaldehyde polymers, polyarylates, polyimides, polybenzimidazoles, polybenzoxazoles, polyphenylquinoxalines, polyoxadiazoles, polycyanates, etc., as well as polymers containing boron, silicon, phosphorus, or sulphur). Korshak and his coworkers[60–67] have used these polymers to develop new thermostable antifriction materials possessing several valuable properties.

A. Carbon-chain Polymers

1. Polyphenylenes[65,88,91]

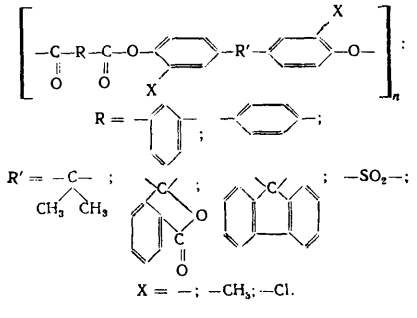


2. Phenolphthalein–phenol–formaldehyde polymers[66,70,82,91]



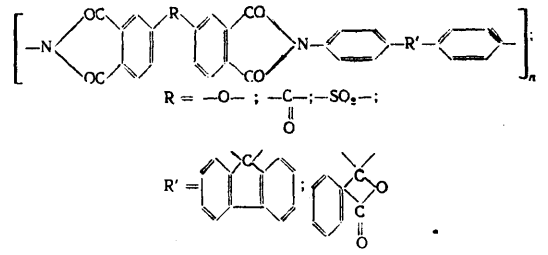
B. Heterochain Polymers

1. Polyarylates[71,72,81,82,91]

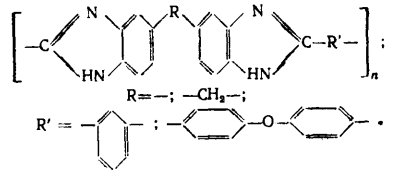


C. Heterocyclochain Polymers

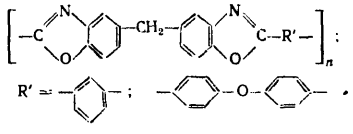
1. Polyimides[71,74,82]



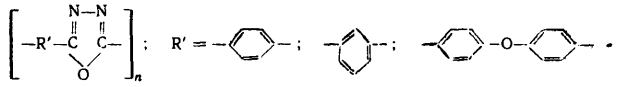
2. Polybenzimidazoles[73]



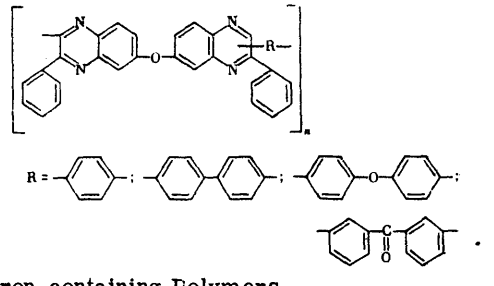
3. Polybenzoxazoles[91]



4. Polyoxadiazoles[60]

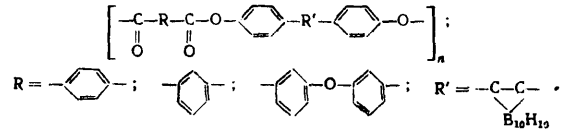


5. Polyphenylquinoxalines[74,79,87,90]

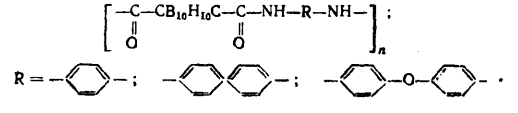


D. Boron-containing Polymers

1. Polyarylates[68,75,93–96]

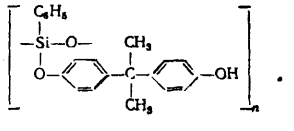


2. Polyamides[68,75,93–96]

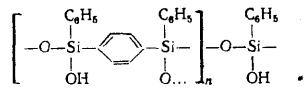


E. Silicon-containing Polymers

1. Polymer B-1[63]

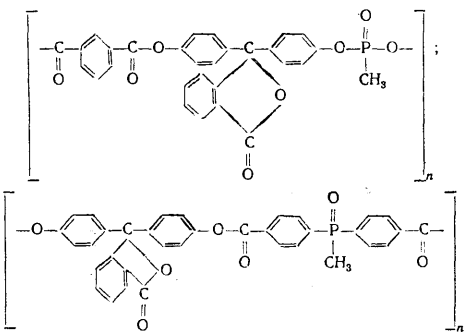


2. Polyphenylenephenylsiloxane[76,91]



F. Phosphorus-containing Polymers

1. Polyesters[78,81,91]



Substantial attention was paid to the behaviour of filled polymer systems during friction at high temperatures and to revealing the role of the polymeric binder, since under these conditions the system undergoes considerable changes in physicomechanical and antifriction properties[80–86]. Studying the thermal friction properties of several thermostable polymers—polyarylates, polyimides, a phenolphthalein-phenol–formaldehyde polymer—filled with molybdenum disulphide, Korshak et al. have shown[81,82,91] that all the filled polymers have a common type of temperature dependence of the coefficient of friction characterised by several friction zones— respectively of minimum coefficient, increasing coefficient, unstable friction, and decreasing coefficient[82] (Figs. 1 and 2)— rapid growth in the coefficient being observed considerably below the glass point of the polymers.

Investigation over a wide temperature range of the relaxation and thermal cohesive properties of self-lubricating antifriction plastics based on polyarylates and polyimides has shown[82] that the temperature limits of variation in these properties coincide with the temperature boundaries of the friction zones. Analysis of the behaviour in thermal friction tests of many filled systems based on polymers of diverse chemical structure, study over a wide temperature range of the relaxation and thermal cohesive properties of the polymers, and determinations of molecular mass and intrinsic viscosity before and after tests under various conditions suggested to Korshak et al.[82] that the temperature variation of the coefficient of friction is governed largely by the structure and properties of the polymeric binder. On the basis of their results they formulated the main physicochemical requirements to be met by polymers used as binders in the development of thermostable antifriction plastics—high heat resistance, thermal stability, and resistance to thermal oxidation, and absence from the chemical and physical structure of such polymers of mobile fragments capable of passing into a labile state at temperatures below the limit of their heat resistance— which are largely satisfied by polymers whose chains contain rings, bulky side-groups, hetero-groups, polar bonds.

In the development of thermostable self-lubricating materials based on thermoplastic polymers close attention has been paid to the influence of the chemical structure of

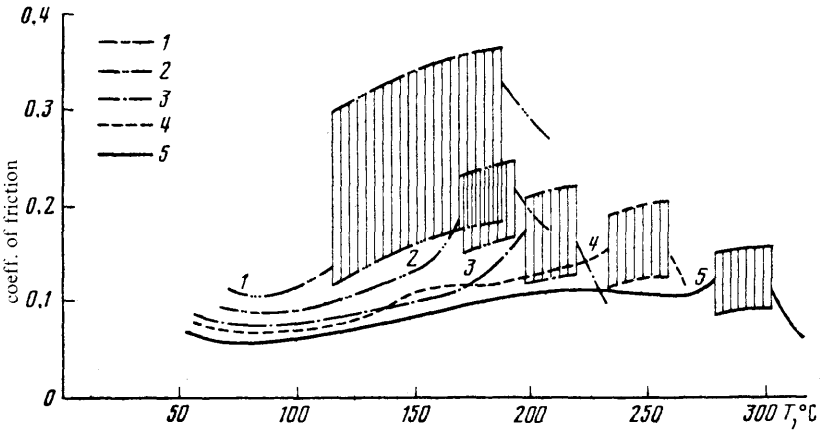
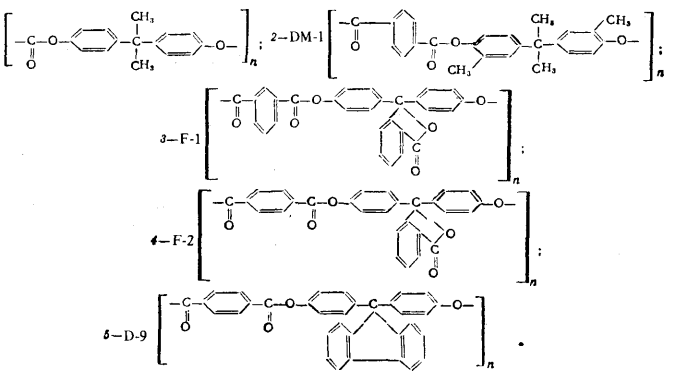


Figure 1. Thermal friction properties of self-lubricating antifriction plastics based on polyarylates of diverse chemical structure: *1*) Diflon.



the monomer unit on the thermal friction properties of the filled systems. With polyarylates of diverse chemical structure as example Korshak et al. [81] have shown that the presence of card [large, planar] groups such as phthalide and fluorene tends to extend the temperature limits of the zone of stable and low coefficient of friction (Fig. 1). Isomerism between dicarboxylic acids (isophthalic and terephthalic acids were used) displaces the "seizing" zone by 30–50 deg to higher temperatures on passing from the *meta*- to the *para*-isomer. Intensifying interchain interaction in the polyarylate macromolecule by introducing polar substituents (chloro) into the aromatic ring system of a diol increases the coefficient of friction of the materials throughout the temperature range. The results indicate that the temperature limits of effective application of self-lubricating antifriction plastics are extended with increase in the rigidity of the polyarylate macromolecules due to increase in the number of aromatic rings, to the presence of card groups[81].

A factor tending to diminish the mobility of the polymer chains is the presence of fused ring systems (benzoxazole, benzimidazole, pyromellitimide) in the monomer unit, which leads to a considerable increase in the heat resistance of polymers. In such polymers the heat resistance usually surpasses the thermal stability, so that in most cases they do not melt, which hinders their processing[58]. In several cases introduction into the chain of mobile units — "hinge" heteroatoms (oxygen, sulphur) bulky substituents, or such hetero-groups as carbonyl and sulphonyl — yields polymers possessing quite high heat resistance while capable of softening below the decomposition point. Fig. 2 illustrates results of thermal friction tests on self-lubricating antifriction plastics based on polyimides containing such "hinge" hetero-groups and -atoms. Comparison of Fig. 1 and 2 shows that such plastics posses higher coefficients of friction than those based on polyarylates, owing to the strong intermolecular interaction of the polymer chains[81,82,91]. The chemical nature of the "hinge" hetero-atom or -group in the monomer unit in the polyimide has a significant influence on the thermal friction properties. Thus the introduction of oxygen atoms into diamine and dianhydride components, by conferring enhanced flexibility on the polymer chain, increases the coefficient of friction and narrows the temperature limits of the zone of minimum coefficient. Increasing the rigidity of the polyimide chain by introducing bridging hetero-groups (carbonyl and sulphonyl) into the dianhydride component or bulky substituents into the diamine component increases the hardness of the material, lowers the coefficient of friction, and extends the temperature limits of the friction zones.

The mobility of the chains can be diminished also by the formation of cross-linked structures. The possibility has been investigated of forming network polymer structures from oligomers (reactophenes, acephenes, phenol-formaldehyde oligomers)[65,66,70,88], from polymers (polyphenylquinoxalines, polyimides)[82,89–91] in the presence of fillers. Korshak et al.[66,82] have shown for a self-lubricating antifriction plastic based on a phenolphthalein–phenol–formaldehyde polymer (FF-40) that the coefficient of friction increases, while wear diminishes, with increase in the degree of hardening of the polymer. The start of the increase in the coefficient at moderate temperatures (~80°C) and within a narrow temperature range (80–90°C) was attributed[66] to the peculiar structure of phenol–formaldehyde polymers, to the presence in the three-dimensional network of two types of junctions — chemical (stable) and physical (labile), formed by hydrogen bonds.

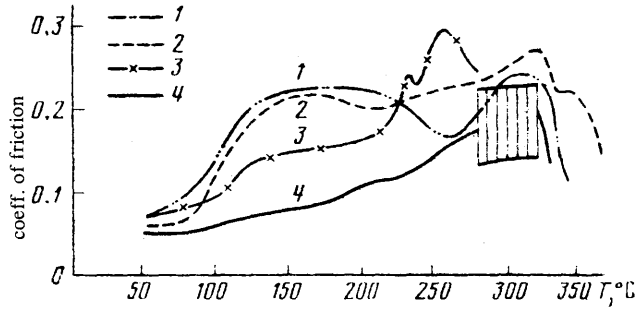
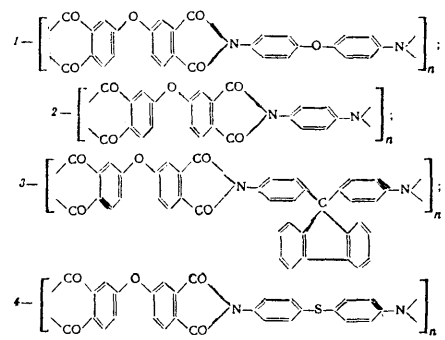


Figure 2. Thermal friction properties of self-lubricating antifriction plastics based on polyimides of diverse chemical structure:



Antifriction plastics based on a slightly hardened polymer exhibit unstable friction and an increase in the coefficient in the temperature range in which the material softens with increase in the thermal cohesive strength. Increase in the degree of hardening of a phenolphthalein–phenol–formaldehyde polymer is accompanied by increase in the viscosity of frictional contact in the zone of incipient softening. However, the cohesive bonding strength is still quite low, so that friction in this zone is stable in character[66].

The use of polymers capable of forming cross-lined structures during processing offers wide opportunities for obtaining new thermostable self-lubricating antifriction plastics with good physicomechanical properties. The possibility of forming a cross-linked structure by means of agents containing reactive groups (terephthalaldehyde, pyromellitonitrile, etc.) has been examined on polyphenylquinoxalines, which are cyclochain polymers; "self-cross-linking" polyphenylquinoxalines, which contain reactive carbonyl groups, have also been used for this purpose[89–91]. Materials based on cross-linked polymers possess a stable coefficient of friction and greater wear resistance at high temperatures.

Considerable attention has been paid to the effect of the chemical nature of the monomer unit in hetero-organic polymers on the antifriction properties[66]. Use of these polymers as binders is not only of theoretical but also of practical interest, since many of them possess high heat resistance and thermal stability, as well as several spe-

cific properties, i.e. incombustibility, radiation resistance, water repellency. The properties of the self-lubricating antifriction plastics are determined not only by the nature of the heteroatom but also by the conditions of formation of the filled system and the chemical structure of the monomer unit[81].

The use as binders of polymers containing carborane groups, which have a considerable effect on the behaviour of the polymers at high temperatures, is of great interest for the production of thermostable self-lubricating antifriction plastics[92–94]. Examination of polyamides and polyesters containing 1,2-, 1,7-, and 1,12-dicarbadodecaborane groups has shown[93–96] that at 400–500°C these polymers form "secondary" structures (pyropolycarboranes), which are thermostable, undeformable, cross-linked polymeric products. The structure and the properties of pyropolycarboranes depend on the method of synthesis, the isomerism of the carborane ring system, and its position in the monomer unit. The strongest tendency to form thermostable, undeformable pyropolycarboranes is exhibited by a polyamide containing 1,7-dicarborane and a polyester containing 1,2-dicarborane in the diol part of the macromolecule. Two types of filled antifriction materials—(*a*) thermoplastic, showing high wear resistance and thermal stability during friction (up to 350°C), and (*b*) cross-linked, undeformable and capable of operating under conditions of dry friction at 350–400°C— can be based on carborane-containing polymers. Korshak et al.[68,75] have used carborane-containing polyamides and polyesters with fillers to obtain new heat-resistant thermostable self-lubricating antifriction plastics that can be employed in dry friction units in the absence of a liquid lubricant up to 400°C. The decrease in the coefficient of friction at 300 to 400°C is largely due to the ability of carborane-containing polymers to evolve hydrogen at these temperatures[91].

Polymers containing silicon, phosphorus, or sulphur have been used to produce self-lubricating antifriction plastics[63,76,81]. Phosphorus-containing polymers and monomers possess the interesting property that filled systems can be stabilised and modified, which permits considerable extension of the temperature limits of application of the materials.

Great attention has been paid to establishing the relation between the chemical structure of a polymer and the wear resistance of filled systems based on it. Results obtained by Korshak et al.[81] show that the production of thermostable wear-resistant materials is a complicated problem, which cannot be solved merely by using more thermostable binders and fillers, since increasing the rigidity of the polymer chain leads to a considerable increase in the viscosity of the melt and raises the processing temperature right up to incipient thermal degradation of the polymer.

The physical structure of rigid-chain polymers, formed either during synthesis or on subsequent heat-treatment, has a significant influence on thermal friction properties. Korshak et al.[97] have examined polyarylates of different supermolecular structure filled with molybdenum disulphide, and have shown that, because of the greater elasticity and lower hardness of a polymer having a fibrillar structure, the coefficient of friction is higher for such specimens than in the case of a globular structure, throughout the temperature range. The depression of the operating temperature limits under friction conditions for a self-lubricating antifriction plastic based on a polyarylate having a fibrillar structure is due to the greater temperature sensitivity of the more complicated fibrillar supermolecular structures.

Investigation of the influence of supermolecular structure on thermal friction properties when poly-*m*-phenyleneisophthalamide (Phenylone) was used as binder[98] led to the development of novel antifriction plastics based on self-reinforcing polymers having the same chemical structure but differing in type of supermolecular structure, which resulted in an optimum combination of frictional and strength properties[72].

Belyi et al.[99–101] made widespread use of a tribometric method to study the influence of supermolecular structures on the friction of polymers and also to investigate self-lubricating compositions comprising polymers and dry lubricants. These studies make it possible to assess the mechanism of the friction of self-lubricating materials, and the influence of the components, their nature, dispersity, and physicomechanical properties on the frictional behaviour of a composition material.

Thus both the chemical structure of monomer unit and macromolecular chain and the physical structure of the polymers influence significantly the thermal friction properties of filled systems. At the same time the filler also has an important role in determining the structure and the properties of the systems: it should ensure not only good lubricating properties but also adequate strength of the materials[84,86,97,102,103]. The structure and the properties of a filled system depend on both the nature and the quantity of a filler. All materials of various degrees of filling can be divided into two groups with respect to their lubricating power[71,103]: the first comprises self-lubricating antifriction plastics containing at most 15–30% of polymer, which possess a low coefficient of friction (0.04–0.12) and high wear resistance; the second group of specimens, containing >15–30% of polymeric binder, is characterised by an unsteady régime in the case of dry friction and a high coefficient. The boundary of "self-lubricating power" depends on the chemical structure of the binder, and is displaced towards higher polymer contents with increase in the rigidity of the macromolecular chain. Within the limits of "self-lubricating power" all materials possess high wear resistance.

Table 1. Variation of molecular-mass characteristics of polyarylate F-1 during friction of self-lubricating antifriction plastics[138] (conditions of frictional contact: p = 2 kgf cm^{-2} and v = 2 m s^{-1}).

Medium	T, °C	F-1-MoS_2		F-1-MoS_2-Cu	
		M*	$[\eta]$ in C_2HCl_3	M	$[\eta]$ in C_2HCl_3
Argon	~50	14000 (44000)**	0.160 (0.284)**	34500 (27100)	0.356 (0.317)
Argon	120	17500	0.185	28500	0.295
Air	~50	23600 (44000)	0.165 (0.284)	29500 (24600)	0.300 (0.265)
Air	120	24000	0.40	66900	0.265

*Molecular masses M determined from the scattering of light.

**Initial values given in parentheses.

The fillers or solid lubricants[104] used have been molybdenum disulphide[105,106], graphite[107], tungsten disulphide[108], fluorinated graphite[109], metal sulphides[110], boron nitride[111], oxides of lead, molybdenum, cobalt, zinc, tin, copper, and

other metals, fluorides of metals, and other solid materials[112].

In the creation of multicomponent self-lubricating antifriction plastics account must be taken of the complicated chemical and physicochemical processes occurring in the polymeric binder, the fillers, and also the boundary layers in the contact zone between binder and fillers on formation of the filled system. The mechanical characteristics of filled polymers largely depend on the adhesion at the polymer–filler boundary[9,10,15,29,113,114]. The interfacial interaction has a special character[98], apparent in the orientation of thin polymer films along the faces of the filler crystals (molybdenum disulphide). These films are assumed to effect cohesion between the filler crystals. In some cases a film may be several micrometres thick even with a high filler content. The filler may have either a plasticising or a strengthening effect depending on its chemical nature and its content[83].

III. CHEMICAL REACTIONS OF POLYMERIC BINDER AND OF FILLER DURING FRICTION

Modern self-lubricating antifriction plastics are essentially filled multicomponent polymer systems in which solid lubricants are accompanied by various powdered fillers— metal powders, powdered coke, quartz, titanium dioxide, etc. — and also fibrous fillers (cellulosic, asbestos, etc.). During operation both individual components and the antifriction system as a whole undergo chemical and physicochemical changes. The operating temperature limits in friction units are determined both by the chemical structure of the polymeric binder, its heat-resistance and thermal stability, and by the nature of the filler, its dispersity, particle shape, activity towards the polymer, proportions of components, and several other factors[102].

The creation of new wear-resistant thermostable self-lubricating antifriction plastics is impossible without a detailed study of the behaviour of the initial components and the filled systems at high temperatures as well as during friction. Relatively little work has been done on the chemical and physicochemical changes occurring in filled polymer systems during friction at high temperatures: greater attention has been paid to the behaviour of pure polymers during friction.

Study of the mechanism of frictional transfer during contact between a polymer and another polymer, a metal, or another material is of both scientific and practical importance[19,33,34]. During friction between a metal and a polymer the latter is transferred to the metal surface, on which it forms a monolayer[115]. Under heavy-duty conditions metal is transferred to the polymer[116,117]. Sviridenok et al.[118] have used an adhesion–deformation mechanism of frictional interaction of solids[16,25] as a basis for the investigation of transfer between polymers differing in adhesive power and cohesive strength, such as polytetrafluoroethylene, polyethylene, poly(methyl methacrylate), polyhexanamide, and poly(ethylene terephthalate). Adhesive power was assessed from the critical surface tension, which established three characteristic types of contact—non-polar–non-polar (polytetrafluoroethylene–polyethylene), non-polar–polar (polytetrafluoroethylene–poly(ethylene terephthalate), polyhexanamide), and polar–polar (poly(methyl methacrylate)–polyhexanamide). Infrared spectroscopy shows[118] that transfer takes place from a less polar to a more polar polymer, and is accompanied by breakdown of the initial material. At the same time changes occur in the surface layer of the other material. The nature of the interacting materials also has a significant influence on transfer. Thus, when a highly polar polyhexanamide film is used together with polytetrafluoroethylene, a strong, continuous layer of the latter 1 μm thick is formed on the film surface. Increase in the duration of contact and in the loading result in amorphisation of the material owing to breakdown of macromolecules in the surface layer. It is assumed that highly reactive radicals of the type CH_2. .C'H.NH.CO are formed during friction. Other workers have also noted the possibility of the occurrence of free-radical reactions in the course of frictional interaction[116,117].

In the region of contact, processes affecting the properties of the surface layers of the rubbing bodies take place under the influence of friction. In the case of a metal–polymer pair this applies both to the polymer and to the metal. At the site of contact an extremely thin third body is formed, with properties determined by the frictional conditions[23]. Its formation is due to coating of the harder body with a thin layer of the softer material, adsorption of a polar lubricant on the surface, formation of stable chemical compounds, etc.

The deformation and thermal processes accompanying the friction of polymers tend to promote tribochemical phenomena[119,120], complicated multistage processes involving activation of the rubbing surfaces by mechanical deformation (i.e. actually the supply and absorption of mechanical energy) and various physicochemical processes occurring under the influence of mechanical activation, which favour the conversion of mechanical into chemical energy[121]. Mechanochemical reactions occur in stages[117,121–124], involving changes of a morphological, supermolecular character (mechanical disaggregation) followed by changes at a molecular level (mechanical degradation), and such degradation leads to chemical reactions[125–127] determined by the polymer structure. Processes occurring under the influence of mechanochemical factors have been studied in polyamides[128–130], phenol–formaldehyde polymers[129], polyethylene[131–136], poly(ethylene sulphide)[132,133], polyformaldehyde[134], poly(ethylene oxide)[133,137], polystyrene[134–136], and poly(methyl methacrylate)[134–136].

Study of the behaviour of filled polymer systems during friction, especially at high temperatures, has established an interconnection between thermochemical and tribochemical reactions in the polymeric binder and in the filler system[138–142]. The friction of filled self-lubricating antifriction plastics entails formation of surface films of the antifriction material both on the surface of the specimen and on the steel counterbody, between which rubbing then occurs[82,138,139]. The character of the films depends on the conditions of frictional contact. X-Ray diffraction and local X-ray spectroscopy have established[139] that the surface films on the counterbody correspond in chemical composition with the antifriction material. Korshak et al.[139] have examined the behaviour during friction of a self-lubricating antifriction plastic based on a polyarylate, and have shown that the polymeric binder undergoes considerable chemical changes depending both on the conditions of frictional contact (atmosphere, temperature) and on the nature of the fillers. Table 1 shows that the friction in argon of an antifriction plastic comprising F-1 polyarylate (based on isophthalic acid and phenolphthalein) and molybdenum disulphide as filler entails a decrease in the molecular mass of the polymer and a proportionate decrease in the intrinsic viscosity (in comparison with the initial values), which indicates the occurrence of degradative processes in the polymeric binder. In an oxidising environment (friction in air) cross-linking degradative pro-

cesses occur in the polymer, leading to some branching of the macromolecular chains.

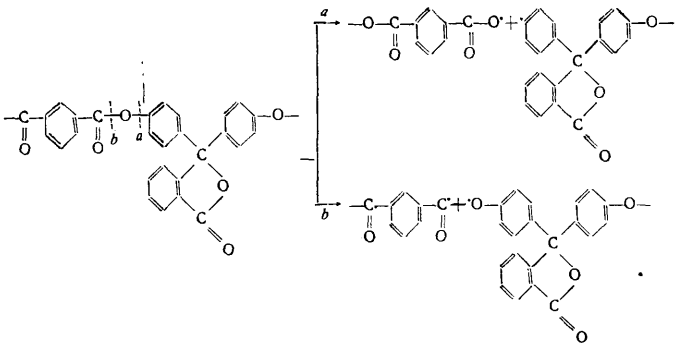
Linear wear on friction is less in argon than in air (Table 2), owing to oxidation of molybdenum disulphide in the latter with impairment of its lubricating properties, as well as mechanical degradation in the polymeric binder. Raising the temperature at the frictional contact intensifies mechanical degradation and diminishes wear resistance of a self-lubricating antifriction plastic comprising F-1 polyarylate and molybdenum disulphide. The presence of copper powder changes the character of the mechanical degradation processes on friction both in argon and in air. When the temperature at the frictional contact is 50° C, cross-linking degradative processes occur in the polyarylate leading to branching and some increase in length of the polymer chain. The wear resistance of the ternary system is greater in argon than in air. Raising the temperature to 120° C intensifies mechanical degradation on friction in air, owing to formation of a partly cross-linked structure. As a consequence the wear resistance of the antifriction material diminishes.

Table 2. Wear resistance of self-lubricating antifriction plastics based on polyarylate F-1 and various fillers[138].

Medium	T, °C	Linear wear, $10^9 I$*	
		F-1-MoS_2	F-1-MoS_2-Cu
Air	50	2.0	1.05
Air	120	3.8	2.2
Argon	50	1.5	0.5
Argon	120	2.7	1.2

*Ratio of height of layer worn away to friction path during surface friction.

Tribochemical reactions in a polyarylate filled with molybdenum disulphide are assumed to occur in argon according to the scheme[139–141]



Increase in the degree of branching of the polymer followed by cross-linking of the macromolecules may occur also as a consequence of cleavage of the lactone ring.

An antifriction filler undergoes considerable changes during the rubbing process, apparent in variation in particle size, some decrease in thermal stability, and chemical interaction with the contacting surfaces and accompanying fillers, which has a significant influence on the lubricating properties of the plastic systems[140]. Thus X-ray diffraction at room temperature has revealed the presence of ferrous sulphide in the surface film formed on the steel counterbody during friction of the F-1–MoS_2 system[139]. When copper is present, however, ferrous sulphide is not detected, owing to the greater strength in this case according to the physicochemical characteristics) of polymer–filler bonding. Infrared spectroscopy, X-ray diffraction, and dynamic thermogravimetric analysis have shown that compounds in which interstitial copper atoms are present in the molybdenum disulphide lattice are formed during friction in the range 110–180° C, with a consequent increase in the coefficient of friction[138,139].

Table 3. Composition of surface films formed on steel during friction of ASP self-lubricating antifriction plastic[138,139] (test conditions: p = 2 kgf cm^{-2} and v = 2 m s^{-1}).

ASP	T, °C	Time, h	Crystallite, Å	Product
F-1-MoS_2	50	2	335	FeS
	120	10	335	FeS
	200	10	430	MoO_2
F-1-MoS_2-Cu	50	2	103	—
	120	2	61	—
	200	10	47	MoO_2, CuS

Raising the temperature at the rubbing contact to 200° C produces a sharp change in the character of the thermal friction curves. Diffractograms of the surface film obtained during friction (Table 3) showed the formation of new tribochemical reaction products. The surface film formed from the F-1-MoS_2 antifriction plastic contained molybdenum dioxide, an oxidation product of the disulphide. Its formation was confirmed by electron diffraction of the film[139]. The presence of copper in the system has a more marked effect on the friction curves at temperatures above 200° C. Tribochemical processes occur more vigorously in the surface films, which contain not only molybdenum dioxide but also small quantities of copper(I) sulphide[138,139].

Thus the composition and the nature of the filler have a significant influence on the formation of surface films when antifriction plastics are subjected to rubbing, and also on the tribochemical reactions occurring both in the polymer binder and in the system of fillers.

IV. PROPERTIES OF THERMOSTABLE ANTIFRICTION PLASTICS

The present Section is a brief survey of the properties and fields of application of a few groups of antifriction materials based on thermostable polymers.

1. Self-lubricating Antifriction Plastics based on Phenol–Formaldehyde Resins

Pheno-formaldehyde resins are widely used as binders in the production of antifriction plastics[66,69,70,143–151]. These polymers find widespread application in industry by

virtue of a combination of valuable properties, primarily thermal stability, heat resistance, and wear resistance[152,153].

Phenoplasts—phenol–formaldehyde resins—are most commonly used with various fillers— such as glass fibre, cotton-wool[154], cotton waste[155], pressboard[156], asbestos fibres[157], etc.— in the manufacture of parts of friction units. Good lubricating properties are conferred on phenoplasts by introducing various solid lubricants, such as molybdenum disulphide, graphite, boron nitride, and polytetrafluoroethylene[158–161]. Another common material for friction units is textolite (resin-impregnated fabric laminate), of which ball-bearing cages and parts for electric motors, pumps, and motor vehicles are made. Textolite is used in friction units with a lubricant. Introduction into textolite of molybdenum disulphide, titanium dioxide, graphite, or selenides or tellurides or their mixtures enables the working capacity of a friction unit to be increased without application of an additional lubricant[162].

Among disadvantages of phenol–formaldehyde resins we must include brittleness and instability towards vibrational overloads; those of reinforced materials based on this thermosetting plastic are low heat conductivity, absorption of several liquids, and high coefficient of thermal expansion.

2. Self-lubricating Antifriction Plastics based on Polyamides

Among heterochain macromolecular compounds the best known as antifriction materials are polyamides[163–167]. These are widely used in mechanical engineering for the production of pinions, bearings[168–170], and cages, as well as various wear-resistant parts[171].

The coefficient of friction of polyamides and their wear resistance depend on the load and the sliding rate[172]. Study of the dry friction of polymers having various chemical structures showed[172] that the coefficient for low-pressure polyethylene increases with rise in temperature less sharply than for polyamides, but for polytetrafluoroethylene it decreases. The type of variation in the case of polyamides was attributed[172] to their structure: the presence of polar groups and hydrogen bonds produces a marked increase in energy of molecular cohesion, which intensifies intermolecular interaction and that between the surfaces during friction, the latter increasing with rise in temperature owing to rupture of the interchain hydrogen bonds of the polyamides. A considerable increase in the coefficient of friction is observed at some "critical" load characteristic of each polymer. With this change in the coefficient with load the polyamide sticks on the steel surface and the intensity of abrasion diminishes. Thus a sharp increase in the coefficient of friction of capron to ~0.9 at a sliding rate of ~1 m s^{-1} coincides with the appearance of adhesion of the polyamide on the steel.

The application of polyamides in pure form as structural materials in friction units is restricted by their strongly hygroscopic character, low heat conductivity (0.25–1.0% of those of metals), large coefficient of linear expansion (9.8×10^{-5}), low hardness, dimensional instability, and moderate load capacity at low temperatures[173,174]. Such defects of polyamides are eliminated by the introduction of various fillers, such as graphite[175,176], molybdenum disulphide[165,176,177], boron nitride, metal powders, fibrous fillers[178], and polytetrafluoroethylene[175,176]. Fillers enhance the rigidity and the compressive strength of polyamides, lower the water absorption and the coefficient of linear expansion, and improve considerably the frictional properties.

Thus the introduction of polyethylene into antifriction compositions based on polyhexanamide helps to separate steel and polyamide surfaces undergoing active molecular interaction and to create under heavy-duty régimes conditions for transition from external to internal friction, ensuring prolonged functioning of the dry friction unit with such operation[179].

An important defect of antifriction plastics based on polyamides is their relatively low heat resistance. The operating temperature range for polyamides is 80–140°C. With rise in temperature the antifriction properties deteriorate continuously. Capron and its compositions can be used[163] in friction units at surface temperatures not exceeding 100°C, P-68 polyamide up to 130°C, and AK-7 mixed polyamide up to 140°C.

3. Self-lubricating Antifriction Plastics based on Polyimides

Among cyclochain polymers polyimides are the most widely used as antifriction materials[71,72,74,180–193]. Aromatic polyimides have very high thermal and thermo-oxidative stability. They can be used at temperatures from −150 to +370°C. Polyimide materials surpass all known plastics in wear resistance, which permits their use in unlubricated bearings. Polyimides are highly resistant to radiation, sunlight, and solvents. Their low volatility in a vacuum makes them promising antifriction materials for use in friction units operating in space. Polyimides filled with graphite or molybdenum disulphide are used for the manufacture of ball-bearing cages[181,189,191,192,194].

Investigation of the influence of moisture on the antifriction properties of a polyimide–steel system shows[195] that entry even of a minute quantity of water is accompanied by a sharp increase in the coefficient of friction and in wear. The variation in the antifriction properties of polyimides and compositions based on them is due to the occurrence of mechanochemical processes at the rubbing surface under the influence of the medium.

4. Self-lubricating Antifriction Plastics based on Epoxy-polymers

Epoxy-polymers are finding increasing application as binders for antifriction materials[196–204]. Bearings based on epoxides are usually employed at temperatures from −50 to +230°C, but under large mechanical loads the upper limiting operating temperature is only 155°C.[153] The fillers generally used in epoxide antifriction materials are graphite, molybdenum disulphide, metal powders and oxides, quartz sand, and also fibrous fillers. An epoxy-plastic filled with graphite or molybdenum disulphide[204] possesses high compressive strength, a low coefficient of friction (0.08–0.09), and heat resistance up to 200°C.

To improve the physicomechanical properties, heat resistance, and lubricating properties epoxy-resins are used in compositions with polyarylates[205], phenol–formaldehyde[206,207] and silicone[200,208] resins, polysulphides[209], or rubbers[210]. A special advantage of materials prepared from epoxy-resins is their ability to harden at room temperature and serve as an antifriction liner.

5. "ASP Plastics"

The scientific principles of the production of thermostable antifriction materials developed by Korshak et al. have enabled several new antifriction plastics to be obtained, among which we must note the "ASP plastics"[211] of various brands (AMAN, TESAN, ESTERAN, VILAN, etc.). These are multicomponent filled systems, in which the binders are polymers possessing a combination of necessary properties— thermal stability, resistance to heat, radiation, and chemical attack, and technical suitability for processing. In their combination of properties the ASP plastics considerably excel known dry friction materials— plastics based on polytetrafluoroethylene and fillers (Table 4).[211]

Table 4. Temperature ranges of application of lubricating materials.

Lubricant	T, °C
Liquid lubricants	−60÷+150
Lubricating greases	up to +180
Polytetrafluoroethylene lubricant	up to +220
ASP plastic	−100÷+300

A distinguishing feature of ASP plastics is their low coefficient of friction and its constancy with variation in temperature. The dependence of the coefficient on the rate of slippage and on the pressure is governed by the ambient temperature. Up to 100°C the permissible loads on these plastics in bearing contact are 100–150 kgf cm^{-2}. The ASP plastics are resistant to benzene, oils, and vibration, are unaffected by moisture, and can be stored for long periods.

The principal use of ASP plastics is as self-lubricating retainers in antifriction bearings, and also as linears in friction bearings. Several standard sizes of ball-bearings with ASP plastic retainers have been designed in the Soviet Union, and introduced into the national economy. The use of such plastics at high temperatures is especially promising. Thus ball-bearings with ASP plastic cages remain in a working state at 250°C after 1000 h operation. These plastics can be used in bearing contact units in which high rates (up to 16 000 rev/min) or high loadings (up to 150–200 kgf cm^{-2}) are required with small rates of displacement of the shaft, and also in cases in which translational motion must be realised after prolonged stationary contact[211]. It is possible to make also ASP plastics pinions bearing a low load, which may ensure high rates of rotation of the shaft.

The superiority of ASP plastics is especially noticeable when they are used in friction units in which other lubricating materials cannot be applied because of high temperatures, radiation effects, or other conditions.

* * *

Thus the above survey makes clear how complicated is the problem of designing antifriction plastics. However, several relations have already been established between the chemical structure of thermostable polymers and the frictional properties of filled polymer systems. This offers wide opportunities for obtaining new materials with specified properties by controlled variation of the chemical structure of the polymer binder.

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Institute of Hetero-organic Compounds, USSR Academy of Sciences, Moscow

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Information

The Ninth International Symposium on the Reactivity of Solids will be held between the 1st and 6th September, 1980, in Krakow (Poland). The symposium is devoted to problems of the mechanisms of reactions in the solid phase. The following questions will be discussed:

1. Defects and transport in solids.
2. Chemical condensation of vapours.
3. The role of the properties of the surface in the reactivity of solids.
4. The formation and transformations of non-crystalline solids.
5. New aspects of phase transformations—the formation of hybrid crystals, non-diffusional transformations, superstructure ordering, etc.
6. The role of solid phase reactions in the development of new technological processes.

A second circular will be sent in 1979.

Translated from *Uspekhi Khimii*, 48, 386 (1979)

The "Nauka" Publishing House is Preparing for Publication a Collection of Articles "Sorbtsiya i Khromatografiya" (Sorption and Chromatography), 20 Sheets, Price 3 Roubles

The book covers various sorption phenomena, surface chemistry, the properties of sorbents, sorption dynamics, and extractive processes. The theoretical articles deal with the phenomenology of sorption processes and thermodynamics; quantum-mechanical calculations on catalyst–adsorbate systems as well as other problems necessary for the understanding of the state of research in the field of sorption are described.

The book is intended for physical chemists working in various fields as well as lecturers and postgraduates at higher educational establishments.

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RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

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The Carbon-Nitrogen Triad Prototropic Tautomerism

B.A.Shainyan and A.N.Mirskova

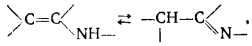
Data on the imine-enamine and related types of tautomerism are surveyed and different approaches to problems of the tautomerism of enamides, which play a major role in biological processes, are examined.
The bibliography includes 98 references.

CONTENTS

I.	Introduction	107
II.	The imine-enamine tautomerism	108
III.	The hydrazone-enehydrazine tautomerism	111
IV.	The tautomerism of certain enamines with *N*-functional group substituents	111
V.	Certain approaches to the problem of the enamide-*N*-acylimine tautomerism	112

I. INTRODUCTION

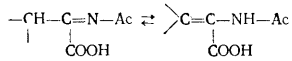
Systematic studies on the carbon–nitrogen triad prototropic tautomerism have been carried out for little more than ten years. As a result of the development of spectroscopic techniques, particularly NMR spectroscopy, quantitative data have been obtained during this period concerning the influence of internal and external factors on the position of the equilibrium



(1)

The major role of unstable tautomeric *N*-acylimino-forms as reactive intermediates has been demonstrated and many reactions have been examined from the standpoint of the involvement of both tautomeric forms. The tautomeric equilibrium constants and the energies of the tautomers have been obtained by kinetic and computational methods.

There has been a considerable growth of interest in the last five years in the study of the enamide–*N*-acylimine tautomerism in connection with research on α-carboxy-enamides (*N*-acyldehydroamino-acids), since it has been observed that such structures are present in natural peptides. A direct relation between the enamide–*N*-acylimine tautomerism



(2)

and the reactions occurring in living organisms (the synthesis and hydrolysis of peptides, the racemisation of natural amino-acids, the metabolism of antibiotics, etc.) has been demonstrated. Methods for the synthesis of penicillins substituted by functional groups at $C_{(6)}$ have been developed on the basis of the formation of reactive intermediate *N*-acylimines.

Bearing in mind the great importance of these studies and the lack of a complete review devoted to the enamine–imine tautomerism, we surveyed the literature published

up to October, 1976, in order to draw attention to this interesting and hitherto little studied field of organic chemistry. Of the earlier publications, we may mention Layer's review[1] of imines in which reactions confirming the possibility of the transformation of imines into enamines are surveyed; there have been no direct observations of the tautomeric equilibrium by physical methods at that time[1].

II. THE IMINE–ENAMINE TAUTOMERISM

Equilibrium (1) has been studied quantitatively mainly for imine–enamine systems and to a lesser extent for iminoesters and hydrazines; there have been only isolated studies on enamines with N-functional group substituents. We shall therefore consider below a quantitative assessment of equilibrium (1) for simple systems and then certain approaches to problems of the tautomerism of enamines with N-functional group substituents.

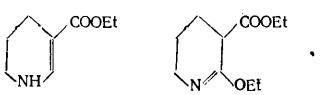
1. The Influence of Substituents in the α-Position

It has been noted in a number of studies that various alkyl substituents in the α-position have a weak influence on the equilibrium position. On passing to aliphatic-aromatic and then to aromatic substituents, the equilibrium usually shifts towards the enamine[2-4], which shows that an α-substituent capable of non-polar conjugation promotes the formation of the enamine (see also Bourbon et al.[5]). However, an approximately 1 : 1 ratio of the two forms for R = CH_3, $CH_2C_6H_5$, and C_6H_5 has been found[6] for the equilibrium

$$C_6H_5-CH=\underset{\displaystyle R}{\underset{|}{C}}-NH_2 \rightleftarrows C_6H_5-CH_2-\underset{\displaystyle R}{\underset{|}{C}}=NH \quad . \qquad (3)$$

The influence of α-substituents is manifested more clearly on passing to α-alkoxyenamines.[7,8]

The introduction of an OR group instead of the hydrocarbon residue into the enamine $C_6H_5CH=C(R)-NH_2$ wholly displaces the equilibrium towards the iminoform[7]; the compound exists as the iminoester $C_6H_5CH_2C(=NH)OR$. The same has been found[8] for the tetrahydronicotinate ester, which exists as the enamine, while its α-ethoxy-derivative exists in the imino-form:



The introduction of a thio-group in the α-position also leads to a high content of the imino-form (up to 70%) [9] (the imino-form is usually absent in the presence of strong electron acceptors in the β-position[4]). When the α-substituents were varied in the system

$$C_6H_5NH-\underset{\displaystyle SR}{\underset{|}{C}}=C(COOEt)_2 \overset{K}{\rightleftarrows} C_6H_5-N=\underset{\displaystyle SR}{\underset{|}{C}}-CH(COOEt)_2 \quad , \qquad (4)$$

a correlation was observed[9] between $\lg K$, on the one hand, and the σ^* constants and the basicity of the enamines on the other: $\lg K = 0.614 - 0.24\sigma^*_R$; $\lg K = -2.992 + 0.34pK_a$. The first expression indicates a very weak dependence of K on the nature of the residue R, which leads to the conclusion that the nature of the atom linked directly to the carbon atom in the α-position has a decisive influence on equilibrium (1).

2. The Influence of Substituents in the β-Position

Substituents attached to the tautomeric centres (i.e. to the β-carbon atom and the nitrogen atom) have a greater influence than substituents at the central atom of the tautomeric system (the α-carbon atom). This is clearly seen from a comparison of the data of Bourbon et al.[5] and Ahlbrecht and Fischer[10]. Thus the content of the enamine form varies from 50 to 67% for α-substituted compounds $CH_3-CH=CRNH_2$ (R = 2-, 3-, or 4-pyridyl), while the variation for the β-substituted analogues is within the wider range from 33 to 100%.[10]

The influence of substituents in the β-position such as NO_2, CN, CO, etc.[4] is such that the imine form is absent. The replacement of the methylgroup in the β-position by the phenyl group also causes a sharp shift of the equilibrium towards the enamine[4,6].

The dependence of equilibrium (1) on the nature of the substituents in the β-position has been studied in detail for a series of enamines $RC_6H_4C(CH_3)=CHNHAr$.[11,12] It was shown that electron-donating substituents shift the equilibrium towards the imine, the shift depending on the solvent: it is greater in polar nitrobenzene than in non-polar bromobenzene.

The introduction of a strong electron-accepting group (R^1 = CN) in the β-position of the iminoesters $R^1CH_2C.(=NR)OR^2$ leads to the appearance of the enamine form, while for R^1 = Ar the compound consists of the pure imine[7].

The increase of the bulk of the R^1_2N group in the enediamines $R^1_2NCH=C(C_6H_5)NHR$ leads to a sharp increase of the content of the enamine and, when R^1_2N = 2,6-dimethylpiperidino, the imine is not detected at all, whereas for $R^1_2N = N(CH_3)_2$ the fraction of the imine is 91%.[13]

3. The Influence of Substituents at the Nitrogen Atom

Analysis of the influence of substituents at the nitrogen atom on equilibrium (1) is of greatest interest, because it makes it possible to build a logical "bridge" from the imine–enamine systems which have been fairly thoroughly investigated to the enamide–N-acylimine system which have been little studied but are extremely important.

The study of the equilibrium (5)

$$R-CH=CR^1-NHC_6H_4-X \rightleftarrows R-CH_2CR^1=N-C_6H_4-X \qquad (5)$$

showed[4] that electron-donating substituents X in the benzene ring shift the equilibrium towards the imine form. The sensitivity to this influence increases in polar solvents (DMSO > pyridine > CCl_4).

An analogous relation for N-aryl-substituted tautomeric systems has been found also in a number of other studies[12,14-16]. N-Alkyl substituents shift equilibrium (1) towards the imine form compared with aromatic substituents[11,14,15]. This permits a conclusion important for subsequent exposition: the conjugation of the lone electron pair of the nitrogen atom with the substituent displaces equilibrium (1) towards the enamine tautomeric form.

A qualitatively analogous picture has been obtained for equilibrium (6)[2]:

$$(CH_3)_2CH-\underset{\displaystyle R}{\underset{|}{C}}=NR^1 \rightleftarrows (CH_3)_2C=\underset{\displaystyle R}{\underset{|}{C}}-NHR^1 \quad . \qquad (6)$$

The authors[2] analysed the relation between the equilibrium position and the π charge on the nitrogen atom in the imine form. A satisfactory correlation has been

observed between the imine content and the π charge on nitrogen: the greater the π charge, the smaller the imine content in the equilibrium mixture.

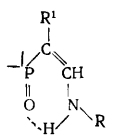
An attempt has been made[3] to find a relation between the content of the enamine and its pK_a. A parallel variation of these quantities has been observed qualitatively although no correlation could be found. Nevertheless, one may conclude that the greater the mobility of the proton in the amino-group the greater the shift of the equilibrium towards the enamine. Since any tautomeric prototropic equilibrium is always displaced towards the less acid form, one may reach an important and unexpected conclusion on the basis of the results of Savignac et al.[3]: the CH acidity of the imine increases to a greater extent than the NH acidity of the enamine as the electron-accepting properties of the substituents at the nitrogen atom are enhanced.

Apart from the electronic effects one should also note the influence of steric factors on the position of equilibrium (1). An increase of the bulk of the substituent R in the enediamines $R^1_2N-CH=C(C_6H_5)-NHR$ leads to an increase of the content of the enamine[13].

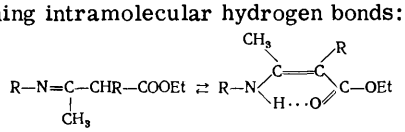
In contrast to the above data, the introduction of aromatic substituents at a nitrogen atom instead of aliphatic substituents in β-phosphorylated enamines

$>P(=O)CR^1=CHNHR$ shifts the equilibrium towards the

imine form; in the R = Ar series electron-accepting substituents in the ring displaces the equilibrium in the same direction[17-19]. Unfortunately the authors do not explain this contradiction between their data and literature results, although they do note a feature of the structure of enamines—the presence of an intramolecular hydrogen bond (IAHB):



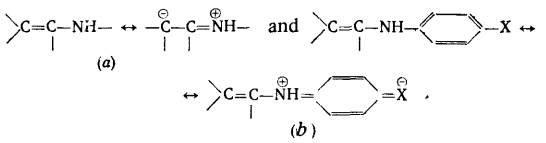
Yakimovich and coworkers[20,21] investigated other systems containing intramolecular hydrogen bonds:



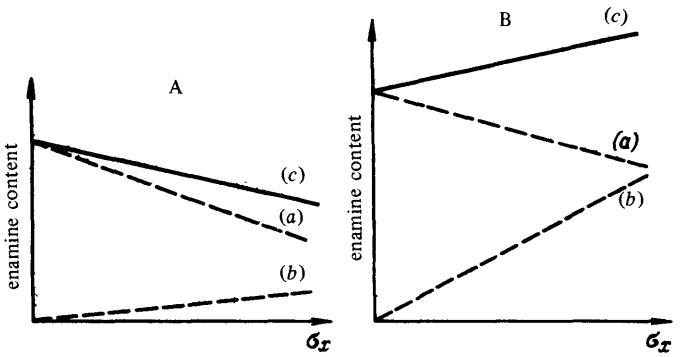
(7)

and also found a situation which is the opposite of that for enamines without such bonds. The authors explained this finding by the fact that the equilibrium position for simple imine–enamine systems[2,4,11-14] is determined by the stability of the enamine form, while in the presence of an IAHB[17-21] it is determined by the stability of the imine form, because the benzene ring in the enamine is not conjugated with nitrogen for steric reasons. The conjugation of the lone electron pair of the nitrogen with the benzene ring is easier than the conjugation of the C=N bond, so that in the absence of an IAHB the electron-accepting substituents stabilise the enamine form to a greater extent than the imine form and displace the equilibrium towards it. In the presence of an IAHB the conjugation in the enamine vanishes and electron acceptors stabilise only the imine, shifting the equilibrium in its direction.

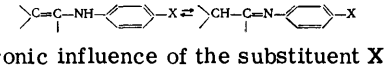
We believe that the simplest and convincing explanation of the unusual behaviour of systems containing electron-accepting groups (C=O, P=O, etc.) in the β-position has been given by Walter and Meyer[22], who considered two mechanisms of the stabilisation of the enamine:



Electron-accepting substituents in the benzene ring promote stabilisation via mechanism (*b*) and act against stabilisation via mechanism (*a*). In the presence of strong electron-accepting groups in the β-position, where the mechanism (*a*) should play an important role, electron-accepting substituents at the nitrogen atom therefore decrease the stability of the enamine and displace the equilibrium towards the imine, which has in fact been observed for such systems[17-21]. This is illustrated graphically in the Figure. The straight line (*c*), which summarises the influence of the substituent at the nitrogen atom on both stabilisation mechanisms [(*a*) and (*b*)], has a negative slope for strong electron-accepting substituents in the β-position. As their electron-accepting properties are weakened, the contribution to stabilisation via mechanism (*b*) increases and the slope of line (*c*) diminishes. This is consistent with the results of other studies[2,4,11,12,14-16].

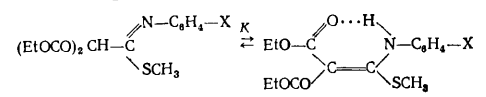


Dependence of the position of the equilibrium



on the electronic influence of the substituent X [22]: A) in the presence of strong electron-accepting substituents in the β-position; B) in the absence of such substituents.

To confirm their conclusions, Walter and Meyer investigated[9] the equilibrium



(8)

and found the following correlation with a negative slope ρ

ρ : $\lg K = 0.534 - 0.61\sigma_X$ ($r = 0.994$; $s_0 = 0.03$).

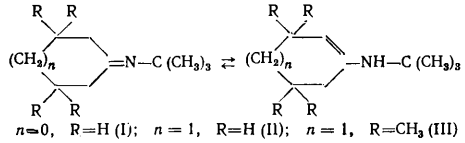
4. The Influence of the Solvent

Two tautomeric forms $C_6H_5-CH(CH_3)-N=C(CH_3)-CH_2COOEt$ and $C_6H_5-CH(CH_3)-NH-C(CH_3)=CHCOOEt$, which form an equilibrium mixture after standing for a

time, were isolated separately in one of the early studies[23]. Equilibrium is established faster in non-polar solvents than in polar solvents. Compared with methanol, pyridine displaces the equilibrium towards the enamine, while acetic acid displaces it towards the imine, which has been explained[23] by the greater basicity of the imine form.

A shift of equilibrium towards the enamine has been observed in many instances in polar solvents: in nitrobenzene relative to bromobenzene[11] and in DMSO relative to benzene [10] or carbon tetrachloride.[24] Ahlbrecht[25] showed that the content of the enamine $CH_3NHC(C_6H_4NO_2) = CHC_6H_4NO_2$ in the tautomeric mixture increases in the following sequence of solvents: $CHCl_3 < C_6H_6 < CH_3NO_2 < CH_3CN <$ acetone $<$ pyridine $<$ DMSO. Evidently a single monotonically varying characteristic cannot be isolated in the above series; this is understandable, because the equilibrium position is influenced both by the solvent polarity and by the ability of the solvent to form hydrogen bonds, as well as other types of specific solvation. Studies on iminoesters showed[7,26,27] that DMSO displaces the tautomeric equilibrium towards the enamine relative to nitrobenzene or dimethylformamide (DMF). The imine–enamine equilibrium constant for the imines $RCH_2CR^1{=}NR^2$ increases on passing from carbon tetrachloride to pyridine and then to DMSO.[4] In other cases the equilibrium also shifts towards the enamine in polar solvents (DMSO, nitrobenzene) relative to non-polar solvents ($CDCl_3$, CCl_4).[6] An attempt to investigate the influence of the solvent was also undertaken by Savignac et al.[3], but, since the imine form greatly predominates in the mixture (up to 95%) and the solvent has only an insignificant influence, the results are difficult to interpret unambiguously.

The series of solvents corresponding to an increasing content of the enediamine $C_4H_9NH-C(C_6H_5){=}CH-N(CH_3)_2$ in the equilibrium mixture is somewhat different[13]: $C_6D_6 < CDCl_3 <$ DMSO $<$ pyridine. The influnece of solvents on the equilibrium position has been studied for the cyclic five- and six-membered imines (I)–(III) [28]:



$n=0$, R=H (I); $n=1$, R=H (II); $n=1$, R=CH_3 (III) .

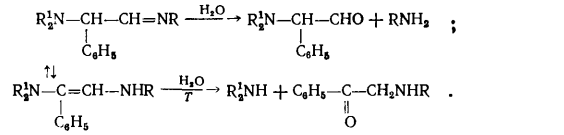
The following series of solvents which cause a shift of the equilibrium to the right has been found for (III): $CD_3OD < CDCl_3 < CH_2Cl_2 < CD_3NO_2 < CD_3CN < C_6H_5NO_2 < CCl_4 < C_6D_6 <$ pure substance $<$ acetone $<$ dioxan $<$ pyridine $<$ DMF $<$ DMSO $<$ cyclohexane. The series is fairly heterogeneous but it is nevertheless possible to distinguish two main tendencies in it: an increase of polarity and of the ability to accept a proton with formation of an intermolecular hydrogen bond (IRHB) from left to right (cyclohexane deviates from this relation). For compounds (I) and (II), the series of solvents investigated are shorter but the qualitative relation is the same.

Hence the ability of the solvent to form intermolecular hydrogen bonds as a rule stabilises the enamine form. The only exception is enamines with an electron-accepting group (C=O or P=O) in the β-position, which gives rise to an IAHB.[17-19]. In these cases solvents forming intermolecular hydrogen bonds disrupt the stable six-membered ring with an IAHB and destabilise the enamine. Thus the compounds $(iso\text{-}C_3H_7O)_2P(=O)CH{=}CH-NHR$ which exist as enamines in carbon tetrachloride, are converted into the corresponding imines in tributyl phosphate[17-19]. Similarly the following series of solvents, increasing the content of the imine form, has been found for equilibria (4) and (8): $CCl_4 \leqslant CDCl_3 \leqslant C_6D_6 < C_6D_5NO_2 < CD_3OD <$ DMSO $<$ pyridine $< CD_3NO_2 \simeq$ acetone.

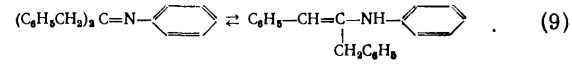
5. The Influence of Temperature

This problem has been studied less than others, although in the investigation of tautomeric equilibria it is very important, since information about the process energetics, the stabilities of individual forms, the entropies of transition of one form into another, etc. can be obtained from the temperature dependence.

The content of the enediamine $C_4H_9NH-C(C_6H_5){=}CH-N(CH_3)_2$ increases from 21% at -25° to 65% at 36°C.[13] This yields the difference between the energies of the tautomeric forms (not calculated by the authors) as $\Delta E = 5$ kcal mole^{-1}, the imine form having a lower energy in this instance. The results of physicochemical analysis have also been confirmed by chemical transformations[13]: hydrolysis to the aldehyde and the amine proceeds in the cold, while on heating the substance is converted into the aminoketone via the following mechanism:



Töke and coworkers[26,27] studied the influence of temperature on the position of the tautomeric equilibrium for iminoesters in DMF and DMSO. $\Delta E = 2.8$ kcal mole^{-1} in DMF and $\Delta E = 4.2$ kcal mole^{-1} in DMSO may be calculated from the data which they obtained. In this case the enamine form is energetically more favourable. An increase of the imine content with increasing temperature was also noted by Ahlbrecht[25]. The following equilibrium in DMSO has been studied over a wide temperature range[24]:



(9)

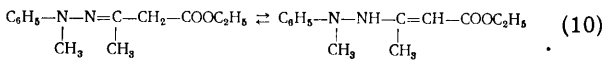
The energy difference (not calculated by the authors) is small (2.3 kcal mole^{-1}), the enamine having a smaller energy than in other studies[25-27]. The temperature dependence of equilibrium (4) has been studied for $R = CH_2C_6H_5$ in $CDBr_3$ and $C_6D_5NO_2$.[29] The parameters $\Delta H^\circ = 3.59$ kcal mole^{-1} and $\Delta S^\circ = 9.35$ cal mole^{-1} K^{-1} in $CDBr_3$ and $\Delta H^\circ = 2.60$ kcal mole^{-1} and $\Delta S^\circ = 6.87$ cal mole^{-1} K^{-1} in $C_6D_5NO_2$ were found; the relative stabilities of the tautomeric forms are analogous to those observed in other studies[24-27].

The influence of paramagnetic additives on the position of the tautomeric equilibrium studied in relation to cyclohexanone imines should also be mentioned[30]. The addition of the europium complex $Eu(fod)_3$ shifts the equilibrium towards the imine, which indicates a greater basicity of the imine form (cf. Potapov et al.[23]). Analysis of the literature data for the tautomerism of simple imine–enamine systems permits certain general conclusions. In the absence of conjugation with an electron-accepting substituent the imine form is more stable. Conjugation with an electron-accepting substituent in any position stabilises the enamine. Solvents forming intermolecular hydrogen bonds displace the equilibrium towards the enamine, apart from the instances where the enamines contain an IAHB; in such systems the solvent has the opposite influence. In the absence of conjugation with electron-accepting groups the imine–enamine equilibrium

constant increases with temperature, while in the presence of such conjugation it diminishes. Finally, the conversion of one tautomeric form into another involves an intermolecular proton transfer, because the intramolecular process is forbidden by the Woodward–Hoffmann orbital symmetry rules[8].

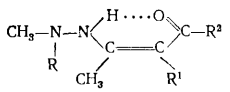
III. THE HYDRAZONE–ENEHYDRAZINE TAUTOMERISM

We shall consider briefly, in addition to the foregoing, the tautomerism of *N*-aminoimines (hydrazones), discovered by Ahlbrecht[31] in relation to the equilibrium



(10)

It has been shown for the compounds $(CH_3)_2NNH-CR^1=CR^2COOEt$ [32] that the conjugation of the group R^1 with the double bond increases the content of the hydrazone (in contrast to simple enamines[2,3,5]). The influence of β-substituents in enehydrazines is the same as in the enamines, i.e. electron-accepting substituents stabilise the enehydrazine. The influence of steric interactions of the substituents R^1 and R^2 in the strained planar structure



has been emphasised[33].

The results of a study[34] where it was shown in relation to the compound $R^1N(CH_3)NHC(CH_3)=CHCOR$ that an enhancement of the electron-accepting properties of the COR residue shifts the equilibrium towards the enehydrazine agree with the data for the influence of β-substituents. A study of the temperature dependence of the tautomeric equilibrium constant for the phenylhydrazone of acetoacetic ester[35] showed that the enehydrazine form is energetically more favourable (as should in fact be the case in the presence of an electron-accepting group in the β-position). The energy difference between the tautomeric forms, which is 2.5 kcal mole^{-1} in C_6D_5Br and 4 kcal mole^{-1} in DMSO, can be calculated from the temperature dependence of the composition of the tautomeric equilibrium mixture. In contrast to these data (as for the imine–enamine systems), in the absence of an electron-accepting group in the β-position, the hydrazone[36] or semicarbazone[37] form is energetically more favourable according to the results of quantum-chemical calculations (the Hückel method).

The shift to the enehydrazine form in DMSO compared with C_6H_5Br is consistent with data for the influence of the solvent (see Section II).[35] Overall, in the absence of electron-accepting substituents, hydrazones are more stable than the tautomeric enehydrazines, the difference in stability being greater than in an imine–enamine system[20,21,32].

IV. THE TAUTOMERISM OF CERTAIN ENAMINES WITH *N*-FUNCTIONAL GROUP SUBSTITUENTS

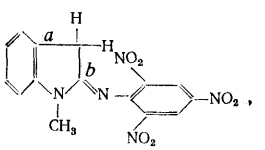
Few studies have been made on the tautomerism of the enamines $\diagdown\!\!\diagup C=C-NH-X$, where X = COR, SO_2, COOR, or another electron-accepting group. One of the first investigations demonstrated the occurrence of tautomerism in *N*-alkoxycarbonylimines[38]. The authors investigated vinylcarbamates $R-CH=CR^1-NH-COOEt$ by infrared spectroscopy and discovered a tautomeric equilibrium involving "iminourethanes" $R-CH_2-CR^1=N-COOEt$ [$R,R^1=(CH_2)_4$(a); $R,R^1=(CH_2)_5$(b); $R=H$, $R^1=C_6H_5$(c)]. The content of the enamide is 67–71% for compound (a), 60–68% for (b), and 31% for (c).

Despite this promising start to studies on the tautomerism of *N*-acylated imine–enamine systems, these data are not very trustworthy. Thus it has been shown[5] that the enamine $CH_3-CH=C(C_6H_5)NH_2$, unsubstituted at the nitrogen atom and having a structure similar to the enamine (*c*), exists in the enamine form to the extent of 92%, although the introduction of the electron-accepting group COOEt at the nitrogen atom should greatly displace the equilibrium towards the enamine, which follows from the analysis of all the available literature data and general considerations. Studies have been made recently[28] also on cyclic enamines analogous to compounds (a) and (b) with a t-butyl group at the nitrogen atom. Even in this instance the content of the enamine reaches 50%, so that it is altogether unlikely that the replacement of the electron-donating t-butyl group by the electron-accepting COOEt group gives rise to a very slight shift of the equilibrium towards the enamine form.

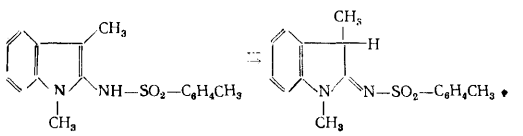
As will be shown below, the available literature data show on the whole that enamines with *N*-functional group substituents exist in the enamine and not the imine form, i.e. when groups of the type C=O, SO_2, and other electron-accepting substituents are present at the nitrogen atom, the enamine form is much more stable than the imine form.

For example, it has been shown[39] that nitriles, which do not have an α-hydrogen atom, combine with triethylsilane, giving rise to aldimines $R-CH=N-Si(C_2H_5)_3$ ($R = t\text{-}C_4H_9$ or C_6H_5). In the presence of an α-hydrogen atom aldimines rearrange almost wholly to the enamines $RR^1C=CHNHSi(C_2H_5)_3$.[40] When $R = R^1 = C_4H_9$, for example, the content of the imine form is only 4.

Interesting studies on indole derivatives have been made by Bailey and coworkers[41,42]. The imine structure has been found for *N*-methyl-2-(*N*-picrylamino)indole in the crystalline state[41]:

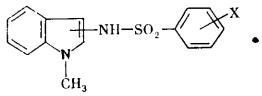


This was done in a fairly unusual way—by X-ray diffraction analysis involving a comparison of the bond lengths *a* and *b*; they are virtually the same (1.52 ± 0.005 Å). On the other hand, in solutions, this compound exists as an enamine (in different solvents). The same workers investigated also 1,3-dimethyl-2-tosylaminoindole, which exists in equilibrium with tosylimine[42]:

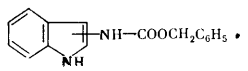


As for imine–enamine systems, in $CDCl_3$ this equilibrium is displaced towards the imine, while in DMSO it is displaced towards the enesulphamide.

The analogous 2- and 3-substituted indoles have been investigated[43,44]:

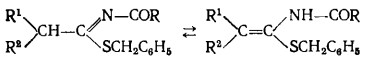


It was shown that the 3-substituted indole exists solely in the enesulphamide form, while the 2-substituted indole exists predominantly in the imine form. The equilibrium was found to be displaced towards the sulphonylimine when electron-accepting substituents X are introduced into the benzene ring. The sensitivity to this influence is small and independent of the solvent. In pure DMSO the content of the enesulphamide is higher than in the mixture of DMSO and 15% $CDCl_3$. *N*-Acyl-derivatives have been synthesised for comparison[43]:



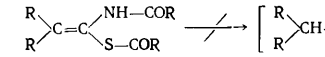
Regardless of the position of the substituent, these compounds exist solely as the enamides. The difference in the behaviour of 2- and 3-substituted enesulphamide isomers can be explained by the fact that the lone electron pair of the nitrogen atom in the α-position with respect to the sulphamide group in the 2-substituted isomer stabilises the sulphonylimine form; such stabilisation is impossible for the 3-substituted isomer. The above explanation has been confirmed by data[45] demonstrating the existence of the compound $R_2NC(CH_3)=NSO_2Ar$ (R_2N = morpholino) only in the form of the sulphonylimine.

α-Thio-substituted enamides have been studied in detail in a series of investigations by Walter and coworkers[46-48]. In contrast to the oxygen analogues iso-C_3H_7-$C(OCH_3)$=N-COR,[49] *N*-acyliminothioesters are in equilibrium with the enamides:



This is apparently due to the greater electron-donating capacity of the lone electron pair of the oxygen atom compared with that of the sulphur atom. The dependence of the equilibrium position on the nature of the groups R, R^1, and R^2 and on the solvent has been studied and the kinetics of the tautomerisation reaction have been investigated by ^{1}H NMR. The reaction was found to be of first order. Analysis of the authors' data leads to the following main conclusions: the change from R = CH_3 to R = C_6H_5 causes a very marked displacement of the equilibrium towards the *N*-acylimine form; electron-donating substituents in the β-position also stabilise the *N*-acylimine; DMSO in most cases causes a complete displacement of the equilibrium towards the enamide form relative to $CDCl_3$.

A further enhancement of the electron-donating properties of the α-substituent leads to a complete displacement of the equilibrium towards the *N*-acylimine. Thus acyliminodithioesters $C_6H_{11}CH_2C(SSR^1)$=NCOR exist entirely in the *N*-acylimine form[47]. The replacement of the cyclohexyl residue in the β-position by the phenyl group leads to the stabilisation of the enamine as a result of the conjugation of the double bond with the aromatic ring and the compound is the enamide $C_6H_5CH=C(SSR^1)NHCOR$. The replacement of the acyl group COR in this compound by the SO_2CH_3 residue leads to its complete conversion into the sulphonylimine $C_6H_5CH_2C(SSR)=NSO_2CH_3$ [47] (in agreement with the results of the study of Harmon and coworkers[43,44] on the relative stabilities of the enamide and enesulphamide systems). A weakening of the electron-donating capacity of the thio-group in the α-position destabilises the *N*-acylimine group and the ketene *S*,*N*-acylals are not converted into the tautomeric *S*,*N*-diacyliminothioesters[48]:



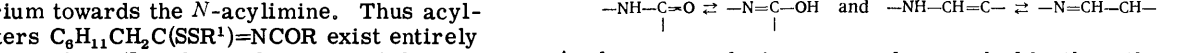
Thus one may conclude that the presence in the α-position of substituents exhibiting an appreciable +*C* effect (for example, OR, SR, and NR_2) is a necessary (but not sufficient!) condition for the appearance of the imine tautomers of enamides or enesulphamides.

V. CERTAIN APPROACHES TO THE PROBLEM OF THE ENAMIDE–*N*-ACYLIMINE TAUTOMERISM

As shown in the previous section, there have been rather few direct studies on enamide–*N*-acylimine tautomeric mixtures. On the other hand, this important problem is directly related to research fields such as transformations of antibiotics, the hydrolysis of peptides, transformations of optically active aminoacids, etc. In contrast to the enamine–imine tautomerism, the enamide–*N*-acylimine equilibrium is in most instances pseudomeric, i.e. is wholly displaced towards the enamide form. This hinders a direct study of the enamide–*N*-acylimine equilibrium and, on the other hand, justifies indirect approaches involving the acylation of tautomeric imine–enamine mixtures, the study of the reactivity of enamides, etc., which will be considered below.

The first major study on vinylcarbamates and vinylureas was published by Sato[50] as early as 1961. The study of the infrared spectra under different conditions led to the conclusion that vinylcarbamates unsubstituted in the α-position do not isomerise to *N*-acylimine, while α-substituted derivatives do isomerise. Such isomerisation of vinylureas proceeds even with the unsubstituted compounds and takes place very readily with α-substituted derivatives. A deficiency of Sato's study is that only infrared spectroscopy was used to demonstrate the structure; this method is not suitable, because the assignment of the bands in the range 1640–1700 cm^{-1} to the C=O, C=N, and C=C groups is fairly difficult for enamide–*N*-acylimine tautomeric systems and one is hardly justified in reaching any quantitative conclusions.

Ultraviolet spectroscopy has been used to study divinylurea $[(C_6H_5)_2C=CH-NH]_2CO$.[51] This compound has a maximum at 318 nm in the ultraviolet spectrum. When one of the nitrogen atoms is methylated, a 40 nm hyspochromic shift is observed, while methylation of both atoms entails a 51 nm hypsochromic shift, which the authors explain by the impossibility in the latter case of tautomerism of two types:



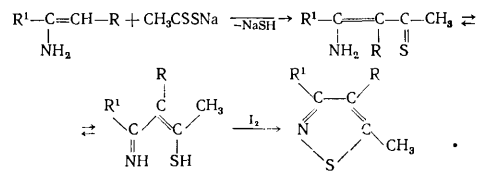
Analogous conclusions were also reached by the authors in the next investigation[52].

Here a small digression is necessary and the problem of the amide–imidol tautomerism as a possible alternative to the enamide–*N*-acylimine tautomerism must be touched upon. For saturated amides, such tautomerism is indeed sometimes observed if the imidol group is stabilised by substituent effects[53]. However, in the absence of such structural features calculation[54] indicates a much higher energy of the imidol form (by 15–20 kcal $mole^{-1}$), which

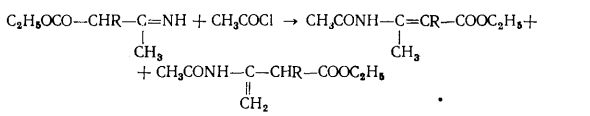
makes it possible to disregard it. So far there have been no comparative calculations of the energies of the *N*-acylimine and imidol forms and our recent calculation[55] for the tautomers $CHCl_2-CH=N-COCH_3$ and $CCl_2=CH-N=C(OH)-CH_3$ showed that the *N*-acylimine form is energetically more favourable than the imidol form to the extent of 16 kcal mole^{-1}.

Goszczynski and Zielinski[56] investigated the acid hydrolysis of *N*-styrylacetamides $CH_3-CO-NH-CR=CR^1-Ar$; it has been shown by infrared spectroscopy that in the protonated form these compounds are *N*-acylimine tautomers $CH_3-CO-NH=CR-CHR^1-Ar$. A similar fact was noted also in an earlier study of the oxidation of imine–enamine systems[57], where it was shown that, when salts are formed, both imines and enamines give rise to imine salts†.

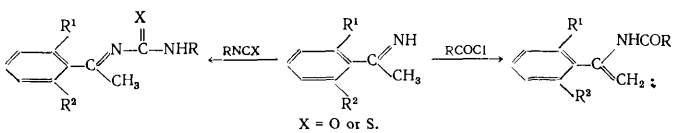
The problem of the enamide–*N*-acylimine tautomerism has also been studied by investigating the acylation of imine–enamine tautomeric mixtures. Such studies were published ten years ago, that of Crenshaw et al.[58] on the thioacetylation of enamines being one of the first. By oxidising with iodine the product of the interaction of CH_3CSSNa with the enamine, the authors were able to isolate an isothiazole, which is formed via the following mechanism according to their view:



When cyclohexanone and isobutyral imines are acylated by acyl chlorides, isocyanates, and isothiocyanates,[59] the products are the tautomeric enamides or enethioamides and not *N*-acylimines. When the $H_2NCR=CR^1R^2 \rightleftharpoons HN=CRCHR^1R^2$ tautomeric mixture is acylated, only the enamide is again formed[6]. Attempts have likewise been made to obtain *N*-acylimines by acylating imines. For aliphatic imines, such an attempt was unsuccessful—the authors[60] obtained the two isomeric enamides:

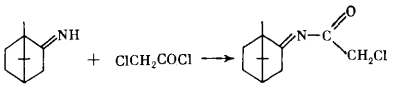


The reactions of acetophenone imines with isocyanates or isothiocyanates yielded *N*-acylimines, while those with acyl chlorides gave enamides[61]:

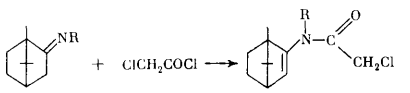


X = O or S.

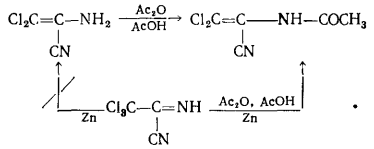
The yield of the *N*-acylimine increases with increasing branching of the substituents R^1 and R^2. *N*-Acylimines are formed more readily by reaction with isocyanate than by reaction with isothiocyanate. Thus, for $R^1 = R^2 = CH_3$, treatment with RNCS yielded the enamide, while treatment with RNCO gave rise to the *N*-acylimine. The *N*-acylimine was also obtained by reaction with chloroacetyl chloride[61]:



The stability of the *N*-acylimine is in this case apparently related to the greater stability of the exocyclic double bond, although in principle the double bond can be converted into a ring[61]:



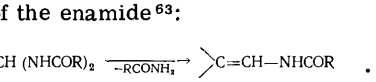
The following transformations have been described in connection with a study of chloral derivatives[62]:



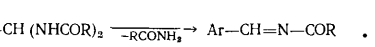
Evidently, both the enamine and imine give rise to β,β-dichloro-α-cyanovinylacetamide.

Thus *N*-acylation of enamines always results in the formation of enamides, while *N*-acylation of imines sometimes gives rise to *N*-acylimines, although the tautomeric enamides are again more frequently produced.

The greater stability of the enamide form compared with the *N*-acylimine form may be inferred also from the results of the elimination of amides from alkylidenebisamides.[63,64] If there is a hydrogen atom in the β-position relative to the amido-group, the elimination proceeds with formation of the enamide[63]:

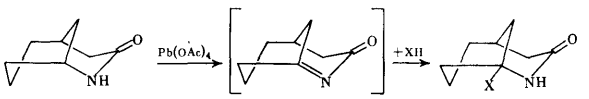


If such a hydrogen atom is absent, the elimination process proceeds under more severe conditions and *N*-acylimines are formed[64]:

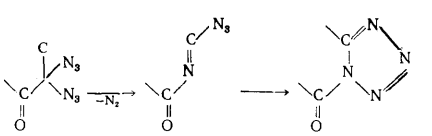


Studies which demonstrated the formation of an unstable tautomeric *N*-acylimine form as the reactive intermediate belong to another series of investigations associated with the problem of the enamide–*N*-acylimine tautomerism. Almost all studies in this group have been carried out in the last five years.

For example, the oxidation of a bicyclic lactam proceeds via the *N*-acylimine[65]; the intermediate *N*-acylimine readily combines with nucleophiles:

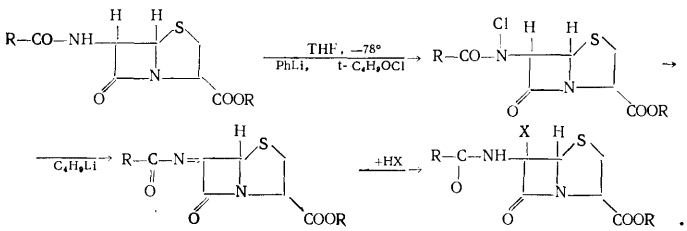


Many photochemical reactions of amides[66] and azidoketones[67,68] involve the formation of intermediate *N*-acylimines. The *N*-acylimines formed in the reaction can readily combine with alcohols[66], can be isolated in a free state[68], or, as in the case of diazidoketones, are converted into tetrazoles[67]:



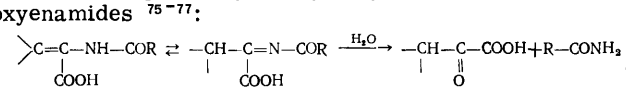
†However, one should bear in mind that the same cation is obtained on *N*-protonation of the *N*-acylimine form and on *C*-protonation of the enamide, so that in this sense the problem of the tautomerism of the initial compounds remains open.

The formation of *N*-acylimines from saturated amides was demonstrated in studies [69,70] where an amide containing a hydrogen atom in the α-position was acted upon by t-butyl hypochloride and an alcohol was then made to add to the *N*-acylimine formed on dehydrochlorination. Using this method, Firestone and Christensen [71] introduced various functional groups in the $C_{(6)}$ position in penicillin:

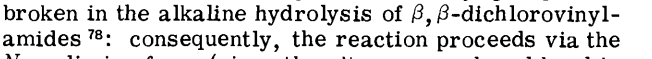


It may be that a study of such reactions will assist a deeper understanding of the metabolism in the living cells of penicillin-based preparations.

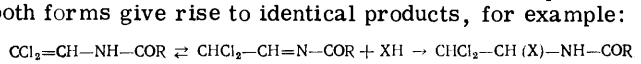
According to the results of Morin and coworkers [72-74], the thermal and catalytic expansion of five-membered O- and S-containing lactams proceeds via the *N*-acylimine form. The formation of the intermediate *N*-acylimine form is accompanied by the hydrolysis of various α-carboxyenamides [75-77]:



The bond between nitrogen and the vinyl group is also broken in the alkaline hydrolysis of β,β-dichlorovinylamides [78]: consequently, the reaction proceeds via the *N*-acylimine form (since the nitrogen–carbonyl bond is broken in the usual hydrolysis of amides):

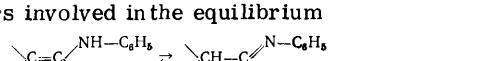


In those cases where the enamide and *N*-acylimine forms lead to different products, it is not difficult to establish the involvement of the *N*-acylimine tautomeric form in the reaction. The situation is more complex when both forms give rise to identical products, for example:

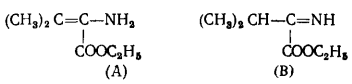


The occurrence of tautomerism in β,β-dichlorovinylamides or their derivatives has been suggested in a number of studies [78-81], but nucleophilic addition to β,β-dichlorovinylamides has been studied quantitatively only recently [82-84]. That the reaction proceeds via the *N*-acylimine form is indicated by data concerning the influence of the catalyst concentration and substituents on the rate of reaction, the presence of the kinetic isotope effect, the reactions with model secondary enamides, etc. The study of the kinetics of the addition of alcohols to *N*-acylimines using the reactions of alcohols with *N*-acylchloral imines, [85] as well as quantum-chemical calculations for individual tautomeric forms and the corresponding common anions [55] made it possible to estimate the tautomeric equilibrium constants (5.7×10^{-4}), the energy difference between the two forms (5 kcal mole^{-1}), and the influence of substituents on the equilibrium position. Electron-donating substituents tend to shift the equilibrium towards the *N*-acylimine form, which agrees well with data for simple imine–enamine systems without a hydrogen bond [4,12,14-16].

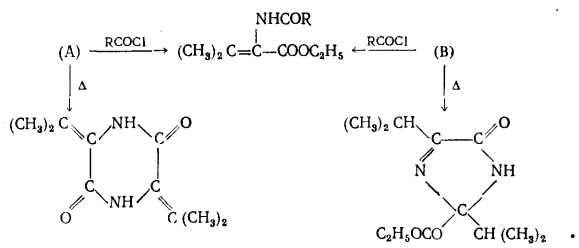
Shin and coworkers [86-90] studied α,β-unsaturated acids and their esters involved in the equilibrium



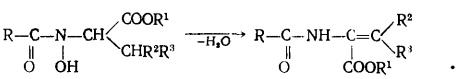
It is of interest that there is no such equilibrium for the analogue unsubstituted at the nitrogen atom—both forms exist individually:



The compounds (A) and (B) give rise to a single enamide on acylation (cf. Refs. 6 and 59) and to different condensation products on heating:

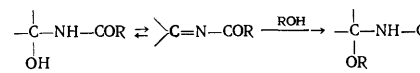


The same workers [87-90] found that, instead of the expected *N*-acylimines, their more stable tautomers (enamides) are formed on dehydration of *N*-substituted α-carboxy-*N*-hydroxyamides:

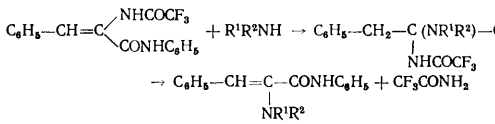


Isomerisation proceeds more readily for $R^2 = H$ than for $R^2 = OCH_3$. [90] This agrees with the general postulate that any electron-accepting influence stabilises the enamine.

Nucleophilic substitution in the α-position of an *N*-substituted enamide also proceeds, according to Meyers and Shaw [91], via the *N*-acylimine (elimination–addition):



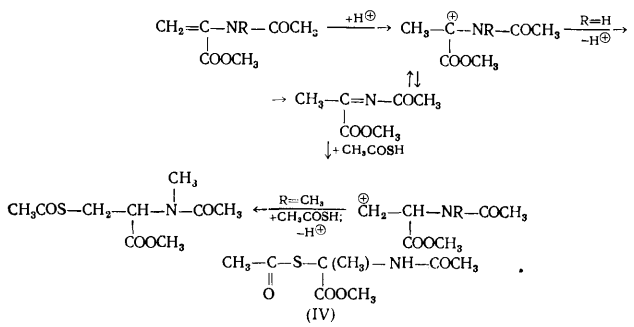
The reactions of a series of α-substituted enamides $C_6H_5CH{=}C(CONHR)NH{-}COR^1$ with mercaptans, amines, and hydrazines were studied recently [92]. The addition proceeds in accordance with the Markovnikov rule; in the case of amines and hydrazine, the reaction continues further:



For hydrazine, the hydrazone form $C_6H_5{-}CH_2{-}C(CONHC_6H_5){=}N{-}NH_2$ is more stable. The formation of the transamination product as a result of addition–elimination has been demonstrated by the absence of reaction for saturated analogues. The authors believe [92] that the addition takes place at the C=N bond of the *N*-acylimine tautomer, because they claim that the addition to the C=C bond of the enamine should proceed contrary to the Markovnikov rule because of the polarisation of the C=C bond under the influence of the carbonyl group. However, the *N*-acylimine form cannot be detected by spectroscopic methods [92].

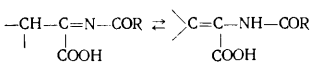
The literature data on *N*-acylimines as the reactive intermediates in the reactions of α-carboxylated enamides have been surveyed to some extent in a brief report [93], which also describes a study of the interaction of α-methoxycarbonyl-enamides with thioacetic acid. The mode of

addition is different for compounds with an NH group and for the *N*-methylated compound. The authors[93] suggest the following reaction mechanism:



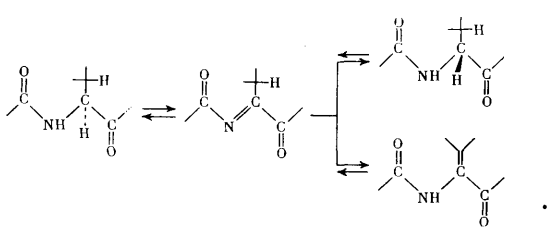
The exchange of the thioacetate group in compound (IV) for the OCH_3 group as well as the reduction of (IV) to $CH_3OCS-CH(CH_3)-NH-COCH_3$ apparently proceed similarly[93].

Studies in which the problem of the enamide–*N*-acylimine tautomerism is considered in relation to the structures of antibiotics, peptides, and optically active aminoacids are of very great interest. Bycroft[94] noted the great importance of the following processes in living organisms:



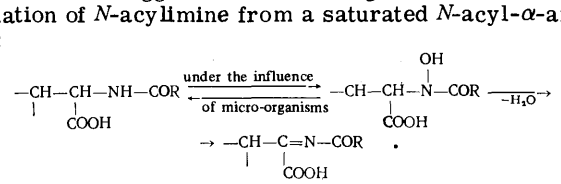
(11)

In particular, Bycroft explains the presence of racemates of aminoacid derivatives in organisms. Since the peptides in living cells are made up of L-aminoacids, D-aminoacids are apparently formed via reversible oxidation-reduction involving *N*-acylimine:



As shown in the scheme above, it may be that the intermediate *N*-acylimine is converted into an enamide. The mechanism illustrated in the above scheme is confirmed by the absence of the D-configuration from the *N*-methylaminoacids, which frequently form part of antibiotics, and by the presence in many peptides of α,β-unsaturated *N*-acyl-α-aminoacids, formed as the tautomers of *N*-acylimines. The above scheme also explains the α-epimerisation rule: if the aminoacid contains more than one chiral centre, the configuration is inverted only at the α-carbon atom. Only one point remains obscure in this scheme—namely why an oxidation–reduction equilibrium occurs at all and what reagents cause it to be established.

Some light has been thrown on this problem by studies[95,96] whose authors suggested the following mechanism for the formation of *N*-acylimine from a saturated *N*-acyl-α-aminoacid:



α-Aminoacids, *N*-acyl-α-aminoacids, and their derivatives $>CHC(COOR)=NR$ and $>C=C(COOR)NHCOR$ have been obtained[96] by a method analogous to that in Refs. 68 to 70. It is seen that here too acylation of imines gives rise to the tautomeric enamides.

Recently there has been a particular growth of interest in α-carboxyenamides (*N*-acyldehydroaminoacids) when it has become clear that they are the starting compounds in the synthesis of peptides[97] and in addition are components of natural peptides[98]. The overall mechanism of the reactions of *N*-acylaminoacids in organisms is as follows[95]: initially biological *N*-hydroxylation and dehydration lead to the *N*-acylimine; in the presence of proton-containing nucleophiles they then rapidly add to the C=N bond, while in the absence of such bonds *N*-acylimines rapidly rearrange to α-carboxylenamides. The addition of peptide residues to the latter also apparently proceeds via the *N*-acylimine form, because the mode of addition is inconsistent with the polarisation of the double bond under the influence of the carboxy-group.

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Investigation of Isotope Effects with the Aid of Kinetic and Catalytic Polarographic Currents

A. Čalusaru

Two types of chemical reactions, used to investigate isotope effects, are considered: reactions preceding the electrochemical stage proper and reactions accompanying this stage. The results of studies on the dehydration of formaldehyde are presented as examples of reactions of the first type and those on the oxidation of titanium(III) to titanium(IV) by hydroxylamine and the decomposition of hydrogen peroxide by catalase are presented as reactions of the second type. The results of a polarographic determination of the rate constants for reactions involving isotopic molecules, on the basis of which it is possible to determine the isotope effect for the corresponding reaction, are described together with the results of the determination of the equilibrium constants with the aid of both classical polarography and oscillographic polarography with rapid potential scanning. The equilibrium constants of the acid dissociation and dehydration reactions involving formaldehyde were determined and were employed to determine the corresponding thermodynamic isotope effects. It is shown that a direct isotope effect obtains in the acid dissociation reaction and the inverse effect obtains in the dehydration reaction.
The possibility of using the results of the study of isotope substitution in relation to catalytic currents in the cobalt-sodium nitrohydroxylaminate-cysteine sytem in an ammonia buffer for the determination of the isotopic composition of water is demonstrated. It is concluded that the polarographic method has many possibilities for the inverstigation of both kinetic and thermodynamic isotope effects and the isotope effects of the solvent.
The bibliography includes 44 references.

CONTENTS

I. Introduction 118
II. Kinetic currents 118
1. Preceding reactions 118
2. Reactions accompanying electron transfer 123
III. Catalytic currents 126

I. INTRODUCTION

The polarographic method makes it possible to determine the rate constant for any chemical reaction, provided that it is coupled with a charge transfer process. Taking into account the sequences in relation to the electrode process, it is possible to distinguish the following coupled reactions: reactions preceding and accompanying catalysis and subsequent reactions. A theoretical analysis has been carried out for all three cases and the tabulated values of special functions make it possible to calculate the corresponding rate constants from experimental data for kinetic waves (a general literature review may be found in the book by Heyrovský and Kuta[1]). If the polarographic method is used to investigate a chemical reaction involving isotopic molecules, atoms, or ions, it is possible to determine the rate constant for the reaction corresponding to the given isotopic species; furthermore, the kinetic isotope effect may be determined from the ratio of the observed rate constants.

The first study devoted to the use of polarographic kinetic currents for the determination of isotope effects was published by the present author in 1965.[2] The decomposition of hydrogen (deuterium) peroxide by catalase in the course of the reduction of oxygen at a mercury dropping electrode was investigated. Later kinetic waves were also used to study certain chemical reactions involving isotopic molecules in light and heavy water[3-5].

Polarographic currents of another type, namely catalytic currents associated with the discharge of hydrogen ions[6-11], were used to study certain special isotope effects[12,13]. Although in this case it is impossible to determine the reaction rate constants from the experimental data, nevertheless the observed isotope effects may be referred to kinetic phenomena, particularly in connection with protonation–deprotonation reactions. In this instance the isotope effect is expressed by the ratio of the numbers of hydrogen and deuterium ions participating in the protonation–deprotonation reaction[12].

This review presents the results obtained in the study of certain typical chemical reactions with participation of isotopic molecules. The classification unsually employed in polarographic studies is adhered to in the description of the results.

II. KINETIC CURRENTS

In order to determine isotope effects, studies were made of only two types of chemical reactions: reactions preceding charge transfer and reactions accompanying this process. However, the number of reactions investigated is very limited in precisely these two instances. The difficulties encountered in the synthesis or deuteriation of large and complex organic molecules may be regarded as the main cause of this situation.

1. PRECEDING REACTIONS

In the determination of isotope effects, we chose only the dehydration of formaldehyde as the preceding reaction[4]:

$$X_2C(OX)_2 \underset{k'}{\overset{k}{\rightleftarrows}} X_2C{=}O + X_2O, \qquad (1)$$

where X is the protium (H) or deuterium (D) and k and k' are the rate constants for the forward and reverse reactions. This process is most characteristic of preceding reactions and makes it possible to determine both thermodynamic and kinetic isotope effects. Among the components of reaction (1), only the aldehydic form X_2CO is

reducing, because the hydrated form [methylene glycol $X_2C(OX)_2$] is not a depolariser. In conformity with Eqn. (1), the dehydration reaction therefore precedes the electrochemical reduction of the aldehyde.

In the first study on the polarographic reduction of formaldehyde, Jahoda[14] found that formaldehyde is reduced to methanol via a two-electron process. This result was confirmed by other investigators[15-18].

The overall electrode reaction may be described as follows:

$$\underbrace{X_2C(OX)_2 \underset{k'}{\overset{k}{\rightleftarrows}} X_2CO}_{\text{chemical stage}} \underbrace{\overset{+2e}{\rightarrow} X_3COX}_{\text{electrochemical stage}} \quad . \qquad (2)$$

The chemical stage may undergo acid–base catalysis and for higher values of pX (pX > 13) account must be taken of the dissociation of the hydrated form. The study of reaction (2) requires the use of certain deuteriated substances. Clearly the most important factor is the preparation of $D_2C(OD)_2$; this substance has been synthesised[4] by the acid catalysis of the exchange of hydrogen bound to the carbon atom. For acid catalysis, solid paraformaldehyde was dissolved in 53% D_2SO_4. A concentrated solution of deuteroformaldehyde was obtained by distillation with dissolution of gaseous formaldehyde in 99.5% D_2O. This solution was redistilled and finally a solution with an overall formaldehyde concentration of 1 M was obtained. NaOD solutions were prepared by the reaction of metallic sodium with heavy water. Deuteriated boric acid D_3BO_3 was synthesised by dissolving boron trioxide in heavy water. The concentration of protons was determined by NMR and proved to be fairly low compared with that in the heavy water usually employed (99.5% D_2O).

(a) Thermodynamic Isotope Effects

In order to determine the rate constant for the chemical reaction preceding the electrode stage proper, it is necessary to know the equilibrium constant for the reaction[1]. As a result of the kinetic effect described by Eqn. (2), it is impossible to determine by classical polarography the equilibrium concentrations of the non-hydrated form of formaldehyde. It is therefore necessary to eliminate the contribution of the chemical reaction itself to the overall current. This problem was solved for the usual non-deuterated formaldehyde by Valenta[19], who used a single-cycle oscillographic polarographic method with a very high rate of change of potential. Using the same procedure, the present author and his coworkers[4] studied systems incorporating both protium and deuterium. i–E curves are presented in Fig. 1 for protium (*a*) and deuterium (*b*); evidently, for a rate of change of potential $s = 4$ V s^{-1} in light water, there is no maximum in the current, while in heavy water there is a small peak, indicating a contribution of diffusion to the reduction of non-hydrated formaldehyde. At a higher rate of change of potential, the diffusional current increases in both light and heavy water. It was found unexpectedly that the diffusion-controlled current in heavy water is reached for lower rates of change of potential than in light water. For very high rates of change of potential ($s = 320$ V s^{-1}, Fig. 1*c*), the maximum currents correspond to the analytical concentration of the free aldehyde form, since the kinetic component has been fully eliminated. Knowing the equilibrium concentration of formaldehyde, it is possible to calculate the equilibrium constant for its dehydration in both light and heavy water.

The concentration of the non-hydrated form in the bulk of the solution can be found from the results obtained by the single-cycle oscillographic polarographic method, treating the height of the diffusion-controlled current peak as a function of $s^{1/2}$ (Fig. 2). For low values of s, the variation of the current is of the kinetic type and the difference between the currents corresponding to systems with light and heavy water is small, while for high rates of change of potential, the difference becomes considerable; as we predicted, the currents are greater in heavy water than in normal water.

The corresponding concentrations of the free aldehydic form can be calculated from the slopes of the straight lines illustrated in Fig. 2. The calculation is possible if it is assumed that the reduction reaction has a

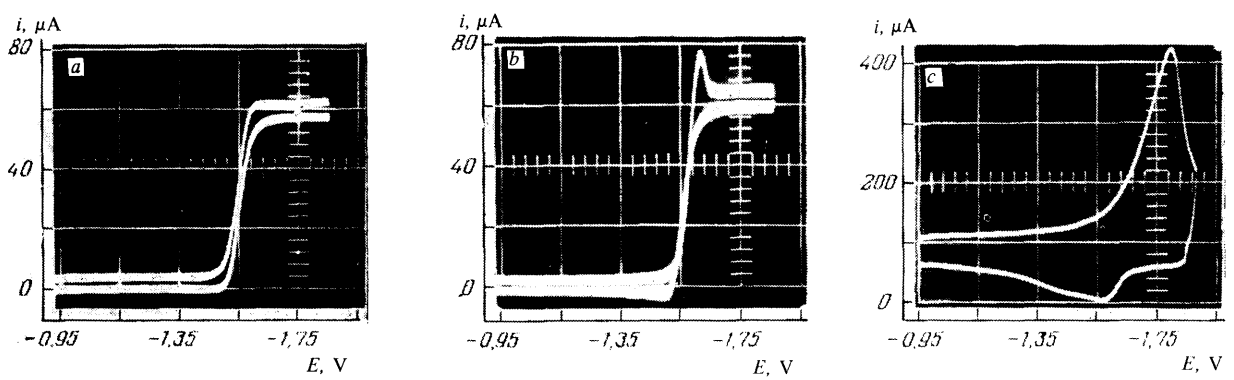


Figure 1. Oscillographic i – E curves for the reduction of formaldehyde at rates of change of potential of 4 V s^{-1} (*a* and *b*) and 320 V s^{-1} (*c*); initial potential −0.95 V; anode–saturated calomel electrode; triangular pulse. Solution: 0.03 M borax and 1.3 M KCl: *a*) 0.217 M H_2CO in H_2O; *b*) and *c*) 0.555 M D_2CO in D_2O. Characteristics of the capillary: $m = 0.227$ mg s^{-1}; $t_1 = 48$ s for $h = 46$ cm (m is the flow rate and t_1 is the drop time).

two-electron mechanism and the following equation derived by Delahay[20] is used:

$$i_p = 3.03 \cdot 10^5 n (\alpha n_\alpha)^{1/2} A D_b^{1/2} c_b s^{1/2},$$

where i_p is the peak current (A), n the number of electrons involved in the overall reaction, n_α the number of electrons involved in the rate-determining stage, α the transfer coefficient, A the drop area (cm^2), D_b the diffusion coefficient of the electrochemically active form ($cm^2\ s^{-1}$), c_b the concentration (mole cm^{-3}), and s the rate of change of potential ($V\ s^{-1}$). The slope, i.e. $\tan\varphi$, can be found from the data in Fig. 2:

$$\tan\varphi = \Delta i_p / \Delta s^{1/2},$$

so that the concentration of the non-hydrated form is

$$c_{b,X_2O} = (\tan\varphi)_X / 3.03 \cdot 10^5 n (\alpha n_\alpha)^{1/2} A D_b^{1/2}. \quad (3)$$

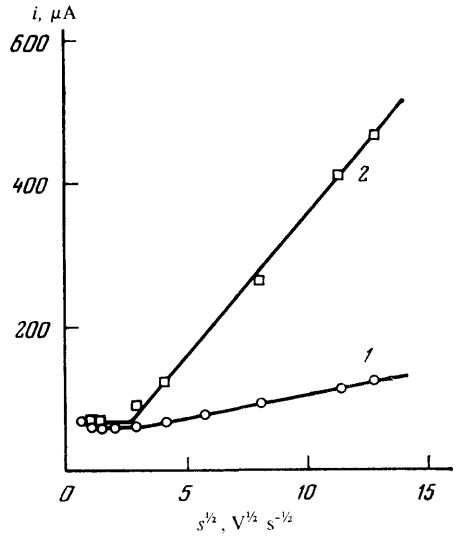


Figure 2. Dependence of the current peak on the rate of change of potential s. Solution: 0.03 M borax and 1.3 M KCl: 1) 0.217 M H_2CO in H_2O; 2) 0.555 M D_2CO in D_2O.

We obtain the following values from Fig. 2: $(\tan\varphi)_H = 6.3 \times 10^{-6}$ and $(\tan\varphi)_D = 41.3 \times 10^{-6}$. Other numerical values are as follows: $n = 2$; $\alpha = 1.48$;[19] $n_\alpha = 1$; $D_{b,H_2O} = 1.22 \times 10^{-5}$ $cm^2\ s^{-1}$;[16] $D_{b,D_2O} = 1.09 \times 10^{-5}$ $cm^2\ s^{-1}$;[21] $A = 2.67 \times 10^{-2}$ cm^2 for the flow rate $m = 0.227$ mg s^{-1} and the drop time $t = 20$ s. On substituting these values in Eqn. (3), we obtain the formaldehyde concentrations $c_{b,H_2O} = 0.94 \times 10^{-1}$ M and $c_{b,D_2O} = 6.4 \times 10^{-4}$ M. The analytical concentrations are $c_{b,t,H_2O} = 0.217$ M and $c_{b,t,D_2O} = 0.555$ M. The equilibrium constants for the dehydration reactions then assume the following values: $K_{h,H_2O} = 4.33 \times 10^{-4}$ and $K_{h,D_2O} = 1.15 \times 10^{-3}$.

The thermodynamic isotope effect can be obtained from the ratio of these two constants:

$$K_{h,H_2O}/K_{h,D_2O} = 0.376\ .$$

Evidently this is in fact an inverse isotope effect, which shows that formaldehyde is more solvated in heavy water than in light water.

This result may be interpreted taking into account the difference between the energies of the chemical bonds of the isotopic molecules. The overall energy of the molecule can be expressed as the sum of the following quantities:

$$E = E_\nu + E_{R,e} + E_{R,i} + E_{Tr} + E_{R,\nu} + E_{El} + E_k,$$

where the subscripts denote vibrations (ν), external rotations (R, e), internal rotation, namely the vibration of a molecule bound to another molecule (R, i), translation (Tr), rotational-vibrational interaction (R, ν), electron shell (El), and atomic nucleus (k).

Analysis of atomic and molecular spectra permitted the conclusion that the difference between the electronic energies of protium and deuterium cannot be responsible for the isotope effect, which exceeds 0.5%. Consequently molecular vibrations may be regarded as the only possible cause of isotope effects[22]. Isotopic molecules have the same chemical formula but, owing to the difference between their masses, their vibration frequencies and "zero-point" energies also differ. A molecule containing a heavy isotope has a "zero-point" energy smaller than the molecule containing the light isotope. Clearly the energy required for the dissociation of each isotopic molecule is different and the difference depends both on the enthalpy and entropy of reaction.

In the formaldehyde dehydration reaction the chemical bond between oxygen and hydrogen is of greatest importance. In water and formaldehyde these bonds are different. In water each molecule has three vibration frequencies, while in formaldehyde their number is greater ($n > 3$). In a water molecule the frequencies ν_i are higher than in a formaldehyde molecule[23]. The zero-point energy is given by the formula

$$E^0 = \sum_{i=1}^{n} \frac{1}{2} h\nu_i.$$

It follows from experimental dehydration constants that

$$E^0(H_2O) - E^0[H_2C(OH)_2] > E^0(D_2O) - E^0[D_2C(OD)_2]$$

or

$$E^0[H_2C(OH)_2] - E^0[D_2C(OD)_2] < E^0(H_2O) - E^0(D_2O) = 3.55 \text{ kcal mole}^{-1}, \text{ (Ref. 21)},$$

Eqn. (4) agrees well with the rule known from isotope chemistry, which states that the heavy isotope enters preferentially the chemical compound in which it is bound more strongly. This rule is applied on the hypothesis that the molecules are in their lowest vibrational energy level and that the entropy change is insignificant.

The hydrogen isotope effect at room temperature depends mainly on the type of chemical bond. The separation fractors, defined as $(D/H)_{compound}/(D/H)_{water}$, are close for compounds with similar bond types. For alcohols, the separation factor depends on the given molecule: whereas for methanol the separation factor is 1.0, for ethanol it is 1.1. In this connection, mention should be made of an important postulate, namely that the greatest isotope effect is noted when the isotopes are considered in compounds where they form a strong chemical bond with a free monatomic element.

We have already noted that, for high pX values, the degree of dissociation of hydrated formaldehyde molecules becomes considerable:

$$X_2C(OX)_2 \rightleftarrows X_2C(OX)O^- + X^+ \quad . \qquad (5)$$

It is possible to calculate the dissociation constant for this reaction, which occurs at high pX values, using the kinetic currents determined by the classical polarographic method.

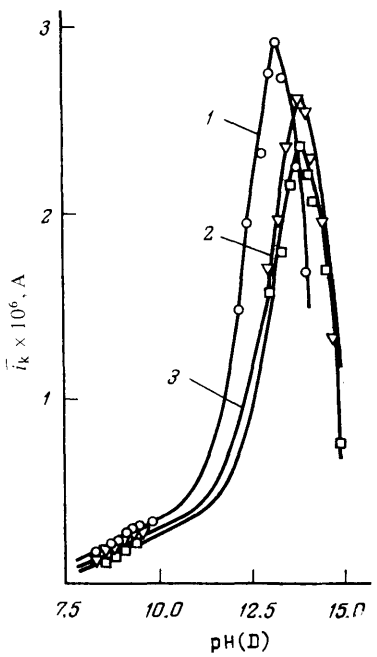


Figure 3. Average limiting current $\bar{i}_k$ as a function of pH(D) for the polarographic reduction of formaldehyde (4×10^{-3} M): 1) H_2CO in H_2O; 2) H_2CO in D_2O; 3) D_2CO in D_2O. A borate buffer was used in the pH range 7.5–10.0 and sodium hydroxide was used in the pH range 10.0–15.0; temperature 20°C.

Fig. 3 [4] illustrates the height of the kinetic waves $\bar{i}_k$ as a function of pH(D) for the reduction of formaldehyde in an alkaline medium. Evidently, in contrast to diffusion currents, kinetic currents are smaller in heavy water than in light water for H_2CO and smaller still for D_2CO. The validity of this result was tested by adding in succession increasing amounts of heavy water at a constant H_2CO concentration and at pH close to the value corresponding to the maximum kinetic current (Fig. 4). Extrapolation of the curve to 100% D_2O agrees, within the limits of experimental error, with the corresponding maximum value on curve 2 in Fig. 3.

In order to determine the dissociation constant K_a for reaction (5), we used the formula derived by Vesely and Brdička[16]:

$$K_a = \frac{[X^+]_M^{1/2}}{[X^+]_M^{1/2} + 2a} ,$$

where $[X^+]_M$ is the H^+ or D^+ concentration for maximum $\bar{i}_k$ (Fig. 3) and a is a constant[16] defined by the formula

$$a = \frac{\bar{i}_k}{(\bar{i}_d)_{b,aq} - \bar{i}_k} [X^+]^{1/2} .$$

Here $(\bar{i}_d)_{b,aq}$ is the diffusion current corresponding to the overall constant concentration of the undissociated form $X_2C(OX)_2$. In the region of low pX values, where the degree of acid dissociation of formaldehyde is very low, the diffusion current corresponds to the analytical concentration of formaldehyde and may be calculated by the Ilkovič equation. Ultimately the following values were obtained[4]: $K_a = 2.5 \times 10^{-14}$ ($pK_a = 13.6$) for H_2CO in H_2O and $K_a = 10^{-14}$ ($pK_a = 14$) for H_2CO and D_2CO in D_2O. The thermodynamic isotope effect is defined as the ratio of these equilibrium constants:

$$K_a(H_2O)/K_a(D_2O) = 2.5 \quad . \qquad (6)$$

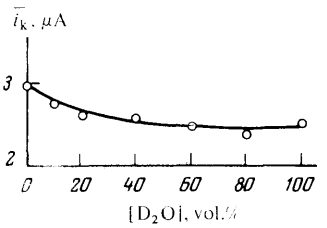


Figure 4. Influence of the content of D_2O on the kinetic current for the reduction of 4×10^{-3} M H_2CO in 0.15 M sodium hydroxide solution (which corresponds to the current maximum in Fig. 3).

In contrast to the dehydration reaction, in the dissociation of formaldehyde the isotope effect is direct, as expected. This result can be accounted for on the basis of the difference between the ionic products of light and heavy water: $pK_{H_2O} = 14.167$ at 20°C [24] and $pK_{D_2O} = 14.963$ at 20°C (calculated from the value of pK obtained by Abel et al.[25] at 25°C). In general the acid dissociation constants of OH, NH, SH, and CH in D_2O are smaller than in H_2O.[26] For weak acids, it has been found experimentally that the ratio K_H/K_D is in the range from 2.5 to 3.9. This agrees well with the value obtained using Eqn. (6) for X_2COXO^-.

(b) Kinetic Isotope Effects

On the basis of data obtained by classical polarography, it is also possible to determine the product of the equilibrium constant K_{h,X_2O} and the dehydration rate constant k_{i,X_2O}. K_{h,X_2O} was defined above and the corresponding rate constant may be found from the formula derived by Weber and Koutecký[27]:

$$\frac{\bar{i}_k}{\bar{i}_d} = \frac{0.886\,(K_h k_i t_1)^{1/2}}{1 + 0.886\,(K_h k_i t_1)^{1/2}} ,$$

where t_1 is the drop time and $\bar{i}_d$ the calculated current determined by diffusion and corresponding to the analytical concentration of undissociated formaldehyde.

The overall rate constant is the sum of the partial rate constants for the dehydration of formaldehyde with participation of water, hydrogen ions, hydroxide ions, and acid (A) and alkaline (B) components:

$$k = k_{X_2O} + k_{X^+}[X^+] + k_{OX^-}[OX]^- + \sum k_{XA}[XA] + \sum k_B[B],$$

In a weakly alkaline borate buffer it is possible to neglect the contribution of the ions X^+ and acid components, and the rate constant is then obtained from a simpler formula:

$$k = k_{X_2O} + k_{X_2BO_3^-}[X_2BO_3^-] + k_{OX^-}[OX^-].$$

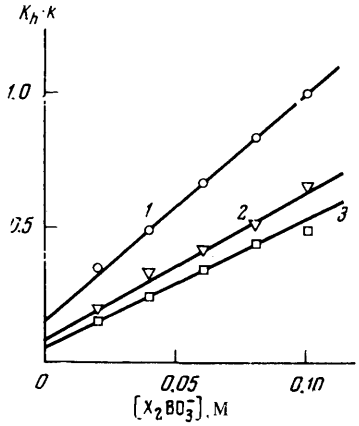


Figure 5. Variation of $K_h k$ with borate concentration. Formaldehyde concentration 4×10^{-3} M: 1) H_2CO in H_2O; 2) H_2CO in D_2O; 3) D_2CO in D_2O; temperature 20°C.

This expression shows that the dependence of $K_h k$ on $[X_2BO_3^-]$ is linear {[the term $k_{OX^-}[OX^-]$ can also be neglected (Fig. 5)]}. The products $K_h k_{X_2O}$ and $K_h k_{X_2BO_3^-}$ can be determined from the intercept made by the straight line on the ordinate axis and from its slope respectively. Their values at 20°C are listed below:

Solution	$10^4 \cdot K_h \cdot k_{X_2O}$, s^{-1}	$10^4 \cdot K_h \cdot k_{X_2BO_3^-}$, litre mole^{-1} s^{-1}	$K_h \cdot k_{OH^-}$, litre mole^{-1} s^{-1}
H_2CO in H_2O	15	8.5	0.279
H_2CO in D_2O	8	5.5	0.6666
D_2CO in D_2O	5.5	4.8	0.496

The corresponding rate constants calculated using the equilibrium constants for the dehydration reaction, determined previously, are:

X	$10^3 \cdot k_{X_2O}$, s^{-1}	$k_{X_2BO_3^-}$, litre mole^{-1} s^{-1}	$10^{-3} \cdot k_{OX^-}$, litre mole^{-1} s^{-1}
H	3.46	1.69	6.44
D	0.478	0.417	4.31

The kinetic isotope effect k_H/k_D assumes the following values at 20°C:

k_i	k_{X_2O}	$k_{X_2BO_3^-}$	k_{OX^-}
k_H/k_D	7.25	4.7	1.5

The maximum theoretically possible kinetic isotope effect for hydrogen isotopes at 25°C is 18,[28] but the experimental values proved to be smaller by a factor of 3. The results can be explained taking into account both the electrode reaction and the reaction medium. Among the three rate constants quoted above, that which corresponds to the solvent (k_{X_2O}) is determined by its nature. In the dehydration of formaldehyde the solvent behaves both as a catalyst and a reactant. A greater isotope effect is therefore to be expected for the rate constant k_{X_2O}, as has been confirmed experimentally. The OH or OD bonds are dissociated in the hydration–dehydration reaction. The maximum theoretical value of k_H/k_D expected for this process at 25°C is 10.6. In practice this value may be largely compensated by other isotope effects. For the given reaction and the constant k_{X_2O} under consideration, the main isotope effect is determined by the transfer of a hydrogen atom and a hydroxy-group from the bound state to water. In order to examine the process more completely, account must also be taken of the changes in the vibration frequency of the system, the anharmonicity of the phenomenon, and the liberation of liquid water molecules.

The isotope effect corresponding to the catalytic constant $k_{X_2BO_3^-}$ probably depends on the dissociation constant of boric acid in light and heavy water. There are no literature data for this constant in heavy water. The relatively high isotope effect is determined by the transfer of a hydrogen ion between the water molecule and the species undergoing reduction, i.e. the process constituting the stage which determines the rate of the entire reaction. This result may be compared with the isotope effect[4,5] in the alkaline catalysis of the ionisation of acetylacetonate[29].

For the constant k_{OX^-}, the isotope effect is determined by the dissociation and hence the strength of the alkali which catalyses the dehydration of formaldehyde. Fig. 3 shows that pD > pH for this process. The relatively small isotope effect in this instance can be accounted for by the two-step mechanism of this reaction. If there is no bond dissociation in the first step, which determines the rate of the entire reaction, and the system undergoes only a slight change, then only a secondary isotope effect of the overall reaction may be noted[30]. A more modern explanation of this mechanism was given by Westheimer[31], who believes that the high asymmetry of the transition state in this reaction, where the proton transfer is the rate-determining step, reduces the isotope effect to a mass coefficient, i.e. $k_H/k_D = 1.4$.

Evidently other chemical reactions preceding the electrode reaction proper can be investigated similarly. Among the substances containing a hydrated aldehyde group and behaving similarly to formaldehyde, mention may be made of the following: pyridine-2-aldehyde, pyridine-3-aldehyde, pyridine-4-aldehyde, glyoxalic acid, pyruvic acid, etc. All these substances have already been investigated in normal water[1]. There also exists a group of substances belonging to the same class, which have not been investigated quantitatively: acetaldehyde, propionaldehyde, glycolaldehyde, alloxan, tetroses, halogenoaldehydes, phthalic aldehyde, and mesoxalic, phenylpyruvic, trimethylpyruvic, and phenylglyoxalic acids.

Another preceding chemical reaction involves the recombination of anions with hydrogen ions. Phenylglyoxalic acid is reducible, while boric acid is non-reducible. The dissociation reactions of complex compounds, among which those of cadmium complexes with nitrilotriacetic acid have been most thoroughly investigated, are analogous. Monosaccharides (particularly aldoses) constitute an important class of organic substances which give rise to kinetic waves. In the study of the isotope effects in all the above instances the greatest

difficulty is the synthesis of the corresponding isotopic molecules.

2. REACTIONS ACCOMPANYING ELECTRON TRANSFER

In contrast to preceding reactions, which the rate constants for the reactions accompanying electron transfer are determined, there is no need to know the equilibrium constants. This facilitates significantly the experiment and classical polarographic data are sufficient for the calculation of the rate constant. In order to determine the kinetic isotope effects, the following reactions have been studied: the oxidation of titanium(III) to titanium(IV) by normal and deuteriated hydroxylamine; similar reactions involving the oxidation of iron(II) to iron(III) and of chromium(II) to chromium(III); decomposition of hydrogen and deuterium peroxide by catalase.

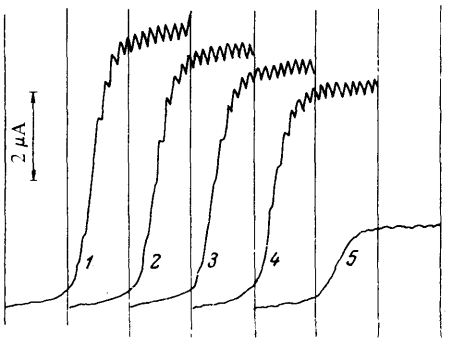


Figure 6. The influence of the concentration of heavy water on the titanium reduction wave in the presence of hydroxylamine; 10^{-3} M $TiCl_4$; 0.2 M $H_2C_2O_4$; 0.0855 M NH_2OHHCl; $[D_2O]$ in 10 ml of solution (ml): 1) 0; 2) 2; 3) 4; 4) 5.8; 5) without hydroxylamine; $t_1 = 3.8$ s; initial potential 0 V; scan along abscissa axis 200 mV; anode–saturated calomel electrode; temperature 24.5°C.

(a) Oxidation of Titanium(III) by Hydroxylamine[3]

In the presence of hydroxylamine the change in the limiting current accompanying the reduction of titanium(IV) to titanium(III) has a kinetic mechanism[32] and is due to the chemical oxidation of titanium(III) by hydroxylamine. The kinetics of this reaction were first studied polarographically by Blažek and Koryta[32]. The rate constant determined by the authors is $k_{25\,°C} = 42.1 \pm 1.5$ litre mole^{-1} s^{-1} and the activation energy is E_H 7.9 kcal mole^{-1}. Delahay et al.[33], who studied this reaction by the chronopotentiometric method, found that the rate constant is $k_{30\,°C} = 30$ litre mole^{-1} s^{-1}. Saveant and Vianello[34] obtained by the same method $k = 42.0 \pm 1.7$ litre mole^{-1} s^{-1}. Using an improved chronopotentiometric method, other investigators[35] found $k_{27\,°C} = 32.0 \pm 2$ litre mole^{-1} s^{-1}. Lingane and Christie[36] used a two-cycle chronopotentiometric method and found $k_{25\,°C} = 43.4 \pm 1.1$ litre mole^{-1} s^{-1} and the activation energy $E_H = 17.3$ kcal mole^{-1}.

In the study of the isotope effect in the above reactions all the substances were deuteriated in the following way: $TiCl_4$ was dissolved in D_2O and deuteriated oxalic acid was then added to the solution. The acid and hydroxylamine were deuteriated by isotope exchange in three successive recrystallisations from 99.9% D_2O. As the heavy water gradually substitutes normal water, the height of the kinetic wave decreases appreciably (Fig. 6). Fig. 7 shows that the dependence of the ratio i_l/i_d on the amount of D_2O is linear (i_l is the limiting current of titanium in the presence of hydroxylamine and i_d is the diffusion current in the absence of hydroxylamine). The kinetic current increases with hydroxylamine concentration and with the ratio i_l/i_d (Fig. 8). It follows from the data in Fig. 8 that, at the same hydroxylamine concentration, the current ratio is always smaller in the deuterium system than in the hydrogen system, but the overall form of the curves is the same in the two systems.

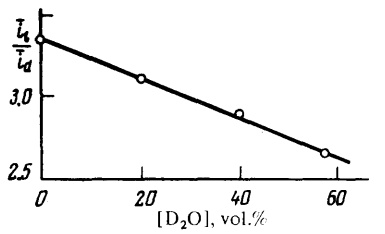


Figure 7. Influence of the concentration of deuterium on the current ratio at 24.5°C.

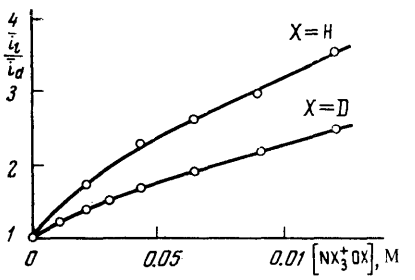


Figure 8. Dependence of the current ratio on hydroxylamine concentration at 23°C.

The kinetic current is determined by the rate of reaction, which explains the rapid increase of its limiting value with increase of temperature. The extent of this change depends on the activation energy, which can be calculated with the aid of the familiar Arrhenius equation:

$$\lg k = -0.43E/RT + \text{const.}$$

Fig. 9 presents plots of $\lg k$ against $1/T$ for the oxidation of titanium(III) to titanium(IV) by hydroxylamine in the hydrogen and deuterium systems. The following activation energies were obtained from the slopes of these straight lines: $E_H = 16.7$ kcal mole^{-1} and $E_D = 17.6$ kcal mole^{-1}; these values are comparable to those published

by Lingane and Christie[36]. It is noteworthy that the activation energies for the hydrogen and deuterium systems are very close, which can be used to elucidate the reaction mechanism.

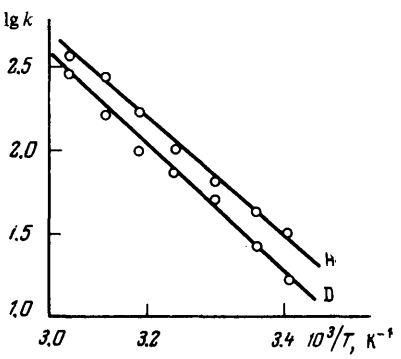


Figure 9. Dependence of $\lg k$ on $1/T$ for the oxidation of titanium(III) by hydroxylamine in the hydrogen and deuterium systems.

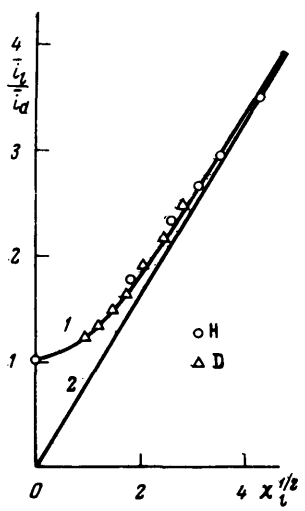


Figure 10. Variation of the ratio $\bar{i}_l/\bar{i}_d$ with $\chi_l^{1/2}$ (curve *1*) and the asymptotic solution (curve *2*); $t_1 = 3.8$ s; $k^H = 41.3 \pm 1.5$ litre mole^{-1} s^{-1}; $k^D = 18.2 \pm 0.8$ litre mole^{-1} s^{-1}; temperature 23 °C.

The following reactions are involved in the given process:

$$Ti^{IV} + e \rightarrow Ti^{III} \text{ (electrochemical stage)}, \quad (7)$$

$$Ti^{III} + NX_3^+OX \rightarrow Ti^{IV} + X_2O + \dot{N}X_2 \text{ (chemical stage)}. \quad (8)$$

The current corresponding to reaction (7) increases owing to reaction (8), which determines the kinetic nature of the limiting current. Since the measurements are made in the presence of an excess of hydroxylamine, reaction (8) is pseudounimolecular and Koutecký's method of calculation[37] may be used to determine the rate constants for the chemical reactions accompanying the electrode process. The calculation shows that the ratio i_l/i_d is a function of χ_l defined by the equation

$$\chi_l = k_X [NX_3^+OX] t_l.$$

The dependence of the ratio i_l/i_d on $\chi_l^{1/2}$ is illustrated in Fig. 10; the experimental data[3] for the oxidation of titanium(III) to titanium(IV) by normal and deuteriated hydroxylamine were used. The calculation yielded the following rate constants at 23 °C: $k_H = 41.3 \pm 1.5$ litre mole^{-1} s^{-1} and $k_D = 18.2 \pm 0.8$ litre mole^{-1} s^{-1}. The kinetic isotope effect is

$$k_H/k_D = 41.3/18.2 = 2.26.$$

The isotope effect in the activation energy for reaction (8), found from the experimental values already indicated, is

$$E_H/E_D = 16.7/17.6 = 0.946.$$

On the basis of the Arrhenius equation in the form

$$k_X = A_X \exp(-E_X/RT)$$

it is possible to determine three isotope effects: in the rate constant, in the activation energy, and in the frequency factor A_X. The first two isotope effects can be calculated from the experimental values of k_X and E_X. The isotope effect associated with the frequency factor A_X can be obtained from the formula

$$\frac{A_H}{A_D} = \frac{k_H}{k_D} \frac{\exp(-E_D/RT)}{\exp(-E_H/RT)} = 1.95.$$

Its value shows that the difference between the rate constants for the reactions of isotopic molecules depends little on the difference between their activation energies. At the same time it is seen that the lower collision frequency in the presence of the heavy isotope leads to a decrease of the rate constant.

The isotope effects in the oxidation of iron(II) to iron(III) and of chromium(II) to chromium(III) by hydroxylamine[5] were determined by the same methods as for the oxidation of titanium(III) to titanium(IV).[3] The reaction medium consisted of an alkaline solution of triethanolamine, which forms complexes with iron and chromium. The test substances were deuteriated as in the case of titanium[3]. Triethanolamine was recrystallised several times from heavy water (clearly only the mobile hydrogen was deuteriated).

The following values were obtained for the oxidation of iron(II): $k_H = 205 \pm 25$ and $k_D = 151 \pm 25$ litre mole^{-1} s^{-1}. Hence the kinetic isotope effect is $k_H/k_D = 205/151 = 1.36$; the activation energies are $E_H = 14.15$ and $E_D = 15.55$ kcal mole^{-1} and the corresponding isotope effect is $E_H/E_D = 14.15/15.55 = 0.909$. This value does not compensate the isotope effect in the rate constant. If the isotope effect in the frequency factor is calculated from the Arrhenius equation, we obtain $A_H/A_D = 1.35$.

The situation is the same in the oxidation of chromium(II) to chromium(III) by hydroxylamine. The observed values are $k_H = 274 \pm 29$ litre mole^{-1} s^{-1} and $k_D = 168 \pm 17$ litre mole^{-1} s^{-1}, $E_D = 12.4$ kcal mole^{-1}, $E_H = 9.74$ kcal mole^{-1}, and the corresponding isotope effects are $k_H/k_D = 274/168 = 163$, $E_H/E_D = 9.74/12.4 = 0.78$, and $A_H/A_D = 1.62$. Hence it follows that the collision frequency plays a decisive role in the kinetic isotope effects for reactions of this type.

(b) Decomposition of Hydrogen Peroxide by a Catalase

In the study of isotope effects the decomposition of hydrogen peroxide by catalase was also examined as a reaction accompanying the electrode process. Polarographic investigation of haemoproteins[38,39] showed that these substances react with the hydrogen peroxide formed in the cathodic reduction of oxygen. One group of haemoproteins reacts with hydrogen peroxide and the resulting compounds can be reduced at potentials intermediate between those of the oxygen and hydrogen peroxide waves. The following haemoproteins belong to this group: haemin[39], haemoglobin, and cytochrome[28]. Catalase differs from haemoproteins by its behaviour[38], because it decomposes hydrogen peroxide. In this process the height of the first oxygen wave increases, while that of the hydrogen peroxide wave diminishes and ultimately the two waves merge into one.

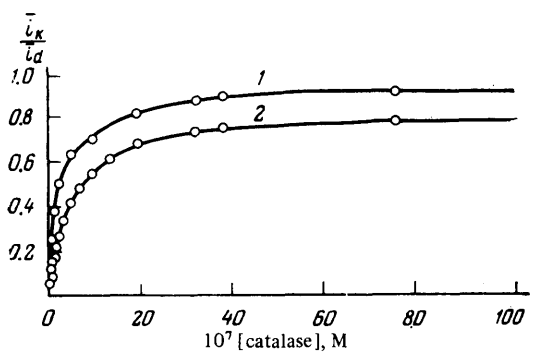


Figure 11. Dependence of the ratio $\bar{i}_k/\bar{i}_d$ on the catalase concentration in Sorensen phosphate buffers in H_2O (curve *1*) and D_2O (curve *2*); pH = pD = 7.2; t_1 = 2.56 s.

Koutecký et al.[40] determined polarographically the rate constants for the decomposition of hydrogen peroxide by catalase. The theoretical interpretation was based on the hypothesis that catalase decomposes into two components the hydrogen peroxide formed during the reduction of molecular oxygen: water and oxygen[2,40]:

$$O_2 + 2X^+ + 2e \rightarrow X_2O_2 \xrightarrow{\text{catalase}} X_2O + \frac{1}{2}O_2 \quad .$$

The study of this reaction in heavy water requires the deuteriation of the test substances[2]. The authors synthesised the deuteriated compounds in the following way. Deuterophosphoric acid was obtained by dissolving P_2O_5 in heavy water and NaOD was synthesised from metallic sodium and heavy water. Since it is clearly impossible to obtain fully deuteriated catalase, we recrystallised catalase twice from a buffer with deuteriated phosphate. In this procedure only the mobile hydrogen was deuteriated. The dependence of the ratio i_k/i_d on the catalase concentration in the range from zero to 1.05×10^{-5} M is illustrated in Fig. 11. Evidently curves having a similar overall shape are obtained in both systems, although the process is slower in D_2O.

The displacement of the second oxygen wave until it coincides with the first wave in the presence of catalase can be accounted for by two causes[41]: the decomposition of hydrogen peroxide by catalase results in the formation of molecular oxygen, which is reduced in the region of the first wave; the hydrogen peroxide formed reacts on the electrode surface with catalase and the resulting compound is then reduced at the electrode, also in the region of the first wave. Koutecký et al.[40] believe that the first mechanism is more probable, since a better agreement can be obtained in this way between the polarographic and oscillographic polarographic methods.

According to this mechanism, the kinetic current $\bar{i}_k$ is determined by the rate of formation of oxygen during the catalytic decomposition of hydrogen peroxide and deuterium peroxide. If the rate constant for the bimolecular decomposition of the peroxides by catalase is denoted by k_X, one can write

$$-\frac{d[X_2O_2]}{dt} = k_X\,[\text{cat}]\,[X_2O_2]_0,$$

and the rate of formation of oxygen is then expressed in the form

$$\frac{d[O_2]}{dt} = \frac{1}{2}k_X\,[\text{cat}]\,[X_2O_2]_0 \,.$$

The rate constant may be calculated from the formula[40]

$$\frac{i_l}{i_d} = 1 + \frac{\chi_l}{7.42 + 1.25\chi_l}, \qquad (9)$$

where

$$\bar{i}_l = \bar{i}_d + \bar{i}_k \text{ and } \chi_l = k_X\,[\text{cat}]\,t_1 \,.$$

The rate constant is then given by

$$k_X = \frac{7.42}{t_1\,[\text{cat}]} \cdot \frac{\bar{i}_k}{(\bar{i}_d - 1.25\bar{i}_k)} \,.$$

Fig. 12 illustrates the dependence of the ratio $\bar{i}_k/\bar{i}_d$ on χ_l. The average rate constants found are[2] $k_H = 1.72\times10^7$ litre mole^{-1} s^{-1} and $k_D = 5.29\times10^6$ litre mole^{-1} s^{-1}. There is good agreement between our value of k_H and that found by Koutecký et al.[40]

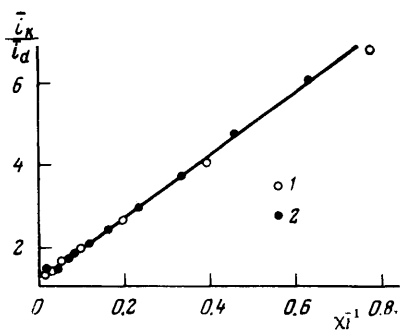


Figure 12. Variation of the ratio $\bar{i}_k/\bar{i}_d$ with χ_l^{-1}; continuous line—calculation by Eqn. (9). The abscissae of the experimental points were calculated from the following values: 1) H_2O_2, $k^H = 1.72\times10^7$ litre mole^{-1} s^{-1}; 2) D_2O_2, $k^D = 5.29\times10^6$ litre mole^{-1} s^{-1}; t_1 = 2.56 s.

Finally the ratio of these constants $k_H/k_D = 1.72\times10^7/0.529\times10^7 = 3.25$ characterises the kinetic isotope effect in the decomposition of hydrogen peroxide by catalase.

III. CATALYTIC CURRENTS

Although the catalytic discharge of hydrogen ions is a very important electrochemical process, the explanation of its mechanism remained for a long time unsatisfactory. The cobalt–nitrohydroxylaminate anion system was the first in which the formation of a cobalt–dinitrohydroxylamine complex, undergoing discharge [oxidation?] and having catalytic properties, was investigated[41]. On the basis of the model of such a dischargeable catalytic complex, mathematical equations were derived for the catalytic waves and a very satisfactory agreement was obtained between the calculated and experimental values[42]. The equations for the catalytic waves in the cobalt–cycloserine system[7,8] were derived on the assumption that the active principle in the catalytic discharge of hydrogen ions is a cobalt complex with a zero charge. In the mechanisms with and without discharge account was taken only of the number of neutralisable protons in a single molecule of the catalyst-complex. Thus the catalytic current depends on the catalyst concentration at the given potential and on the catalytic activity, expressed in terms of the number of protons discharged by a single molecule. This mechanism proved to be useful for the prediction of conditions under which it is possible to obtain the catalytic double wave characteristic of proteins. The equation for the catalytic nth degree wave[6–8,42] suggests that, when the same solution contains two complexes with different catalytic properties, a double catalytic wave will be recorded. The theory was tested experimentally for solutions containing cobalt(III), sodium nitrohydroxylaminate, the cysteine in an ammonia buffer[43].

It is well known that, for substances exhibiting catalytic properties in the presence of cobalt (giving rise to the so called Brdička waves), the height of the hydrogen wave is independent of pressure, in contrast to the nitrohydroxylaminate ion. This behaviour is characteristic of kinetic waves, i.e. waves determined by the chemical reactions accompanying the electron transfer process. However, the study of the cobalt–cycloserine system[7,8] showed that the independence of the overall catalytic hydrogen wave of pressure is due to the superposition of two catalytic hydrogen waves of different types: of the type of the "pre-sodium" wave and the wave determined by diffusion induced by the discharge of hydrogen ions under the influence of the cobalt–cycloserine complex. The resolution of the complex wave into the above components can be achieved at very low cobalt concentrations. At high cobalt concentrations the decrease of the first wave as the height of the mercury column is varied is compensated by the increase of the second. Ultimately the resulting overall hydrogen wave is independent of pressure. Clearly such independence is not evidence for the kinetic nature of the polarographic waves of the Brdička type. Any mechanisms in which such complex waves are assumed to be of the kinetic type must therefore be completely excluded from the interpretation of the Brdička type hydrogen ion discharge process.

Another important type of the catalytic discharge of hydrogen ions was discovered recently[9–11] in acetate buffer solutions containing nickel and selenocysteine[9,10] or normal cysteine[11] as the catalyst in weakly acid or neutral media. Such discharge of hydrogen proceeds in the region of the catalytic pre-wave with a half-wave potential of approximately –1.14 V relative to the saturated calomel electrode (sat.c.e.).[9] It was shown[9] that in this case catalysis is due to the uncharged partly protonated form of the nickel complex of selenocysteine or cysteine.

If the half-wave potential is adopted as a criterion in the classification of the hydrogen ion discharge processes at a mercury dropping electrode, the following waves may be indicated: (1) the catalytic hydrogen pre-wave at –1.14 V;[9] (2) the normal hydrogen wave at –1.67 V;[1,9] (3) the Brdička hydrogen wave between –1.67 and –1.70 V;[6,11] (4) the catalytic pre-sodium hydrogen wave at –190 V (sat.c.e.);[6] (5) secondary discharge of hydrogen ions beginning at –2.63 V (relative to a stationary mercury electrode in 10^{-3} M KCl, after the subtraction of the ohmic potential drop[44]). Thus the discharge of hydrogen ions at a mercury dropping electrode is a fairly complex process.

Since the catalytic discharge of hydrogen ions involves protonation–deprotonation reactions and more or less protonated catalyst molecules in a free or bound form, it follows that the catalytic hydrogen waves should be influenced by the substitution of hydrogen ions by deuterium ions. On the other hand, as shown in the first part of this review, the dissociation constants of normal and heavy water differ. Despite the complexity of the processes occurring in the catalytic discharge of hydrogen, it is possible to characterise the overall isotope effect (I) by the ratio of the numbers of protons (N_H) and deuterons (N_D) discharged by one molecule of the catalytic complex[12]:

$$I = N_H/N_D;$$

N_H and N_D can be calculated from the formulae for the catalytic waves[8,42].

When a non-dischargeable complex or a complex with a zero charge is taken into account in the mechanism of the catalytic discharge of hydrogen ions, the equation for the waves assumes the following form[8]:

$$\bar{i}_t = \frac{\bar{i}_{d,\mathrm{Co(II)}}}{1+\exp[(\varepsilon-\varepsilon_{1/2,\mathrm{Co(II)}})\,\alpha_l n_l F/RT]} + \frac{\bar{i}_{l,\mathrm{H(0)}}}{1+\exp[(\varepsilon-\varepsilon_{1/2,\mathrm{H(0)}})\,\alpha_3 n_3 F/RT]} + \frac{\bar{i}_{l,pv}}{1+\exp[(\varepsilon-\varepsilon_{1/2,pv})\,\alpha_4 n_4 F/RT]} + \bar{i}_{el}\,, \tag{10}$$

where $\bar{i}_t$ is the overall average current, $\bar{i}_{d,\mathrm{Co(II)}}$ the Co(II) diffusion current, ϵ the electrode potential, $\epsilon_{1/2,\mathrm{Co(II)}}$ the experimental half-wave potential of the cobalt wave, α_l the effective transfer coefficient, n_l the valence of the electrode reaction, F the Faraday, and T the absolute temperature; $\bar{i}_{l,\mathrm{H(0)}}$ has the value stated above, but refers to the uncharged zero-valent cobalt complex catalysing the discharge of hydrogen ions. The subscript pv refers to the catalytic pre-sodium wave and $\bar{i}_{el}$ is the current corresponding to the discharge of the ions of the indifferent electrolyte.

The quantity N_X can be calculated from $il,\mathrm{H(0)}$ by Eqn. (10), provided that the concentration of the uncharged complex on the electrode surface is known.

When the complex undergoing discharge is involved in the mechanism of the catalysis of the discharge of hydrogen ions, the equation for the wave can be written in the following form[2,4,6,8]:

$$\bar{i}_t = \frac{\bar{i}_{l,\mathrm{Co}}}{1+\exp[(\varepsilon-\varepsilon_{1/2,\mathrm{Co}})\,\alpha_l n_l F/RT]} + \frac{\bar{i}_{l,k}}{1+\exp[(\varepsilon-\varepsilon_{1/2,k})\,\alpha_2 n_2 F/RT]} + 1 - \frac{1}{1+\exp[(\varepsilon-\varepsilon_{1/2,k})\,\alpha_2 n_2 F/RT]} \cdot \frac{N\,(\bar{i}_{l,k}/n_2)}{1+\exp[(\varepsilon-\varepsilon_{1/2,c})\,\alpha_3 n_3 F/RT]} + \frac{i_{l,pv}}{1+\exp[(\varepsilon-\varepsilon_{1/2,pv})\,\alpha_4 n_4 F/RT]} + X\cdot c\cdot\exp[-(\varepsilon-\varepsilon_{1/2,el})\,\alpha_{el} n_{el}\cdot F/RT]\,.$$

In this equation the subscripts k and 2 correspond to the complex being reduced and c and 3 correspond to the wave associated with the discharge of hydrogen ions by

the catalytic complex; X is the constant of the Ilkovič equation and c is the concentration of the indifferent electrolyte. In practice only the third term of Eqn. (11) need be taken into account in the calculation of N_X. This type of calculation has been carried out for hydrogen[42] and deuterium[12] and for cobalt–cysteine solutions in an ammonia buffer.

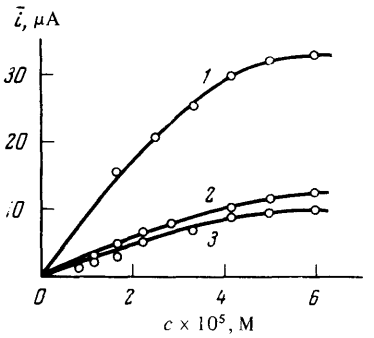


Figure 13. Variation of the height of the catalytic wave with cysteine concentration; 10^{-3} M $CoCl_2$; 10^{-1} M NX_4Cl–NX_4OX: 1) X = H; 2) and 3) X = D; 1) in the presence of 0.01% of gelatin; 3) in the presence of deuteriated gelatin.

A marked isotope effect was shown in the cobalt–cysteine system for waves corresponding to the catalytic discharge of hydrogen ions. As in previous instances, deuteriated compounds are necessary for the investigation of the isotope effect. ND_4OD was synthesised by the reaction

$$Mg_3N_2 + 8D_2O = 2ND_4OD + 3Mg(OD)_2.$$

ND_3 was then separated from $Mg(OD)_2$ by a partition and by bubbling with gases. DCl was synthesised by the reaction

$$SiCl_4 + 4D_2O = 4DCl + Si(OD)_4.$$

$DCl.D_2O$ was separated from $Si(OD)_4$ by the distillation of an azeotropic mixture. (Both ND_4OD and DCl are also available commercially.) The substance ND_4Cl was obtained either by the reaction of ND_4OD with DCl or by isotope exchange between N–H and D_2O with repeated recrystallisations. The mobile hydrogen in gelatin was deuteriated by repeated dissolution in D_2O and evaporation. Cysteine for the deuterium system was recrystallised three times from solution in D_2O.

Waves corresponding to the catalytic discharge of deuterium ions can be obtained with the aid of these deuteriated compounds and compared with the corresponding hydrogen waves. Fig. 13 illustrates the experimental variation of the current maximum on the catalytic waves as a function of cysteine concentration. The currents are much smaller in the D_2O system. $N_H = 740$ and $N_D = 238$ were calculated from the experimental data. Hence

$$I = N_H/N_D = 740/238 = 3.2.$$

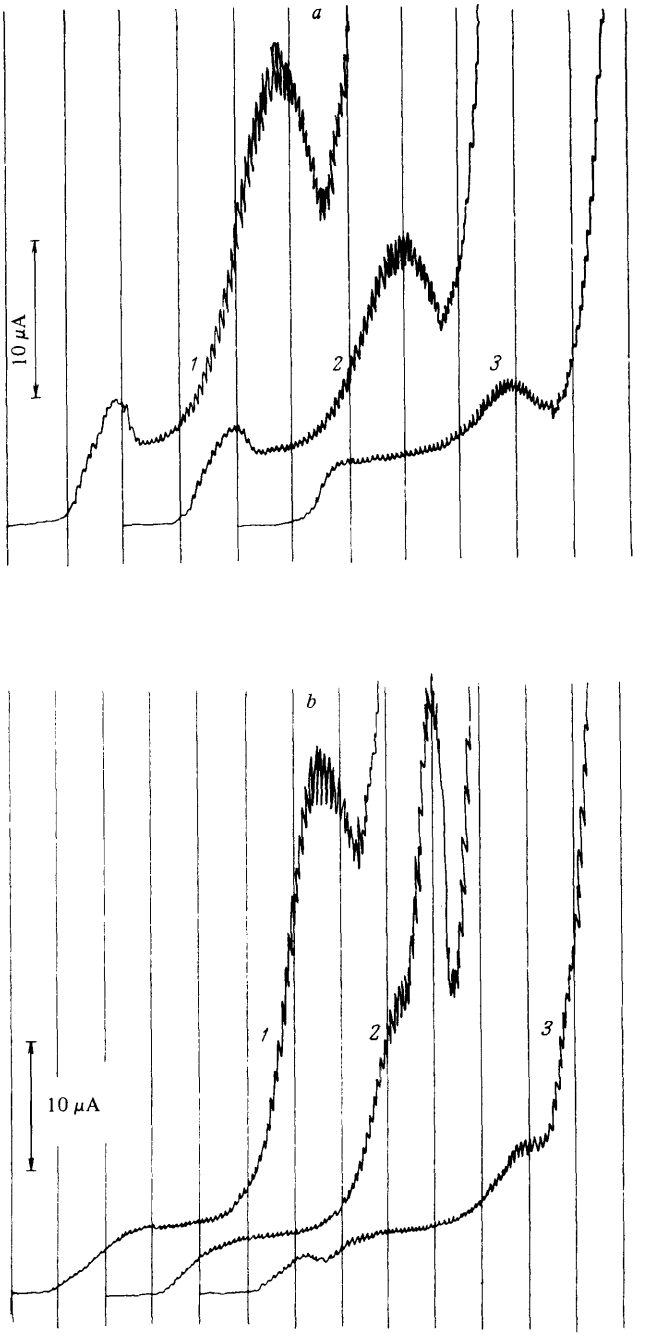


Figure 14. The catalytic isotope effect in the presence of 10^{-3} M Co^{2+} (*a*) and Ni^{2+} (*b*); 5×10^{-5} M (*a*) and 3×10^{-4} M (*b*) cysteine solutions; 0.1 M NX_4Cl; 0.1 M NX_4OX (X = H or D); initial potential −0.8 V (*a*) and −0.4 V (*b*); scan along the abscissa axis 200 mV; anode–saturated calomel electrode; deuterium content (vol.%): 1) 0; 2) 60; 3) 100.

The isotope effect is even greater in solutions containing cobalt or nickel (Fig. 14) in the absence of gelatin. A polarographic determination of the D_2O content in

enriched systems has been suggested as an application of this very intense isotope effect[13]. Calibration plots for the cobalt system are illustrated in Fig. 15*a* and that for the nickel system in Fig. 15*b*. A straight line is obtained when the maximum catalytic current is plotted against the deuterium content. The accuracy of the analytical determinations is equal to the accuracy of the polarographic method (1–3%). An advantage of the method is the simplicity of the procedure and apparatus.

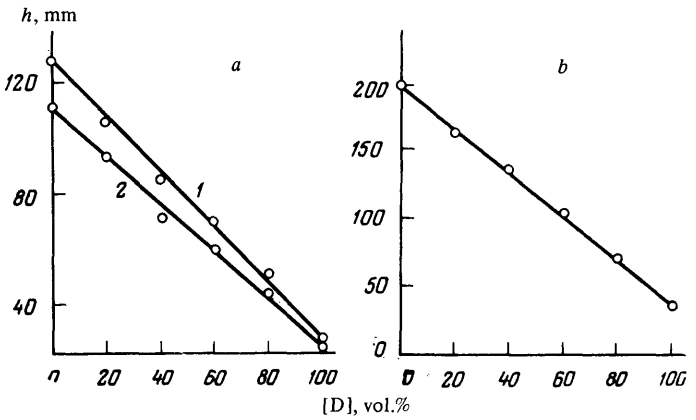


Figure 15. Variation of the height of the catalytic wave (*h*) with the deuterium content in the presence of cobalt (*a*) and nickel (*b*). Solutions the same as Fig. 14: 1*a*) first recording; 2*a*) second recording.

The study of isotope substitution in relation to catalytic currents constitutes an important procedure for the determination of the mechanism of this main type of polarographic currents. The intense isotope effect demonstrates the fundamental role of protonation–deprotonation processes and the importance of this stage, which determines the rate of the overall reaction. Isotope substitution also demonstrates the importance of hydrogen catalysis when other criteria are unsuitable for the determination of the nature of the polarographic wave.

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In conclusion one must emphasise that, despite the complexity of the phenomenon under consideration, the study of the isotope effect with the aid of kinetic and catalytic waves gives rise to much scope for the understanding of the mechanisms of many reactions and at the same time demonstrates the advantages and possibilities of the polarographic method in this field.

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Structural Rearrangements in Carbaboranes and Related Compounds

V.I.Stanko, V.A.Brattsev, and S.P.Knyazev

The rearrangements of polyhedral boron compounds are described systematically and classified. The fundamental characteristics of various types of rearrangements are examined and the relation between them and the electronic structure and symmetry of the molecules is established.
The bibliography includes 191 references.

CONTENTS

I.	Introduction	130
II.	General characteristics of the rearrangements of polyhedral boron compounds	131
III.	Quantum-chemical criteria of the rearrangements	135
IV.	Reductive and oxidative rearrangements	137
V.	Thermal rearrangements	141
VI.	Conclusion	149

I. INTRODUCTION

Rearrangements of atoms and of the molecular skeleton are characteristic of polyhedral boron compounds, particularly carbaboranes. They can take place under both thermal and chemical influences. This review presents a systematic arrangement of studies in this field in order to discover the relation between the chemical properties and the electronic structures of molecules and to establish on this basis the general characteristics of the rearrangement of polyhedral boron compounds†. Data published up to 1978 are used in the review.

From the entire multiplicity of the rearrangements of cyclic and open-chain polyhedral molecules and ions, it is possible to isolate two main groups: (a) rearrangements in which the initial and final molecules (ions) have structures based on the same polyhedron; (b) rearrangement involving a change in the type of polyhedron. The rearrangement of the first type (thermal rearrangements) are characterised by the fact that they are caused by thermal excitation and proceed without a change in the number of electrons between the initial and final systems. The rearrangements initiated by electromagnetic radiation, for example, ultraviolet light, and chemically initiated thermal rearrangements also take place without a change in the type of polynedron. Rearrangements of the second type are characterised by a change in the total number of electrons in the atoms of the skeleton. Depending on whether the rearrangement takes place owing to an increase of the number of electrons in the system or their decrease, it is possible to distinguish reductive and oxidative rearrangements respectively. Reductive rearrangements involve the opening of the polyhedral molecule following the appearance of additional external σ bonds. On the other hand, oxidative rearrangements lead to the closure of the polyhedral molecule or ion.

When the mechanisms of thermally initiated (i.e. without the involvement of chemical reagents) rearrangements of polyhedral compounds are considered, different versions of the so-called *dsd* mechanism (diamond–square–diamond) are most widely used (Fig. 1). This mechanism was proposed by Lipscomb, who used it to account for the rearrangement of virtually all closed polyhedral systems[3]. The second mechanism discussed in the literature is based on the hypothesis that different fragments of the polyhedral molecule can rotate in both the ground and transition states[4-7]. The third type of possible mechanisms, involving *closo*-compounds, is based on the hypothesis that the molecule is opened in the transition state to give a fragment of the next polyhedron and is then reclosed but in a different direction[5,8], while in the case of *nido*-compounds the polyhedral molecule is closed with subsequent opening[9-12]. The lack of adequate experimental data on this problem permits in most cases only a theoretical consideration of various mechanisms of the thermal rearrangements. We believe that the limitations due to the symmetry of the occupied and vacant boundary molecular orbitals can serve as a criterion for the selection of the most probable pathways in the rearrangements (see Section III).

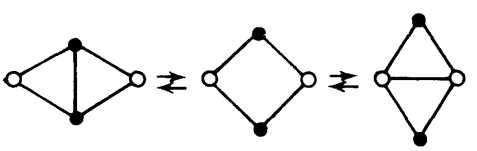


Figure 1. Model of the *dsd* (*diamond-square-diamond*) mechanism.

The rule governing the relation between the type of structure, the class of compound, and the number of electrons binding the skeleton of an n-atomic molecule, which was discovered by Wade, plays an important role in determining the direction of the reductive and oxidative rearrangements: the $n + 1$, $n + 2$, and $n + 3$ electron pairs characterise the *closo*-, *nido*-, and *arachno*-structures. The addition of two electrons to a closed n-atomic polyhedral molecule should lead to its opening with formation

† This review constitutes a stage in the systematic analysis of studies in the chemistry of carbaboranes and other polyhedral boron compounds (this is a development of our previous communications[1,2]).

of the *nido*-structure of a fragment of the next $(n + 1)$-atomic polyhedron; the addition of the next electron pair gives rise to the *arachno*-structure of an n-atomic fragment of the $(n + 2)$-atomic polyhedron, etc.[13] Taking into account the importance of the above features of the chemistry of polyhedral boron compounds, we shall refer to them as the *"Wade rule"*.

As will be shown below (see Sections II and III), a change in the number of electrons and in the general case in the number of orbitals occupied by electrons in the transition stage constitutes the driving force also of a number of thermal rearrangements, including those of closed polyhedral systems. On the other hand, reductive rearrangements are associated with the accommodation of additional electrons in the lowest unoccupied molecular orbitals (LUMO), while oxidative rearrangements involve the removal of electrons from the highest occupied molecular orbitals (HOMO) of the initial molecule. The rearrangement proper proceeds as a spontaneous process or as a process with a low activation energy and in the latter case constitutes in essence a thermal process. Using a particular classification one must therefore bear in mind the limits of its applicability. Although the proposed classification is partly conventional, particularly when the individual stages of the rearrangements are considered, we nevertheless believe that it is useful when the process as a whole is considered.

II. GENERAL CHARACTERISTICS OF THE REARRANGEMENTS OF POLYHEDRAL BORON COMPOUNDS

In many chemical reactions of carbaboranes and other polyhedral boron compounds the decisive role of the characteristic features of the chemical bonds involving the atoms in these compounds is manifested. Analysis of literature data on the structures and reactivities of polyhedral boron compounds enabled us to isolate the following most significant features which determine the feasibility, direction, and mechanism of the rearrangements.

1. The presence of a reactive dynamic electronic system linking the atoms of the molecular skeleton, in the absence of a σ skeleton characteristic of classical carbon compounds.
2. The dependence of the configurational stability of polyhedral molecules on the symmetry of the boundary HOMO and LUMO and the energy gap between them and the consequent relation between the type of the resulting structure of the polyhedral molecule and the number of electrons binding the molecular skeleton (Wade's rule).
3. The reactions of polyhedral compounds with electrophiles involving HOMO and the reactions with nucleophiles involving LUMO.
4. The equal participation of boron and carbon atoms as well as other hetero-atoms in the electronic structure of the skeleton of the polyhedral molecule and the consequent appearance of an excess charge on the heteroatoms (for example, a positive charge on the carbon atoms in carbaboranes) and polarisation of the entire electronic system binding the atoms of the skeleton.

1. THE CHEMICAL BOND IN POLYHEDRAL BORON COMPOUNDS

Two main approaches have now been developed, permitting a description of the valence and electronic structures of the molecules of polyhedral boron compounds: the topological approach[14-17] and quantum-chemical calculations based mainly on the molecular orbital method in various approximations[14,18-29].

The topological approach is based on the idea that a strong two-electron bond may be formed between three atoms, i.e. a three-centre bond[30]. This concept was introduced because polyhedral systems cannot be described solely in terms of two-centre bonds, since in these compounds each boron atom supplies only two electrons for three atomic orbitals involved in the formation of the bonds of the skeleton. In order to describe the polyhedral molecule within the framework of the topological approach, equations are derived for electron balance, charge balance, orbital balance, and hydrogen atom balance. Their solution yields the number of three-centre and two-centre bonds characterising the given system. Next, using a series of topological limitations, topologically allowed valance structures are selected from all the possible combinations. Bearing in mind that formally 2/3 of the electronic charge corresponds to each atom on formation of a closed three-centre bond, a single charge corresponds to each atom on formation of a two-centre bond, etc., the method makes it possible to assess, together with the possible valence structures, also the charge distribution among the atoms of the polyhedral molecule. The topological approach is used to describe the chemical reactions of polyhedral compounds[31,32] and rearrangements[32,33] too. However, we believe that in the given instance the formalism of this method does not permit an understanding of the essential features of the transformations taking place and it is necessary to impose additional boundary conditions on the possible directions and mechanisms of the chemical reactions (see below).

The quantum-chemical calculations for the description of the electronic structures of polyhedral compounds are based on the molecular orbital method, which, being the most general procedure for the description of the chemical bond, makes it possible to obtain quantitative parameters characterising the given molecule. The molecular orbital method is used for the calculations on the ground states, for the determination of the possible directions of the reactions in particular rearrangements, and for the estimation of the stabilities of the intermediate compounds[10,34,35] (for example, in the rearrangement of 1,2-$C_2B_4H_6$ to the 1,6-isomer[36]).

Using the criteria governing the localisation of molecular orbitals proposed in the literature[37-40], Lipscomb and coworkers determined the localised valence structures of many boron hydrides and carbaboranes[23,24,28,29,41-44]. The valence structures obtained by the localisation of molecular orbitals agree on the whole with the topologically allowed structures when one considers in the latter case the set of possible structures taking into account the symmetry of the molecule. The majority of the molecules for which calculations have been made within the framework of the localisation criteria contain atoms whose bonds have minimal electron populations. The concept of a *fractional* three-centre bond was therefore introduced[41] and in the general case the concept of a fractional bond[28]. In order to represent the extent to which the bond is fractional (its population), together with valence bonds represented by continuous lines the following conventional representations have been introduced:

dashed line with an arrow	(·····→)	0.15 - 0.25 e;
continuous arrow	(——→)	0.25 - 0.35 e;
dashed line	(·····)	0.35 - 0.5 e;
continuous line	(——)	0.5 e.

Bonds with populations $< 0.15\ e$ are excluded from consideration[28]. Fig. 2 presents as an example the localised valence structures of 2,4-$C_2B_5H_7$,[24,41,43] 2,3-$C_2B_4H_8$,[24,41,44] $C_2B_7H_{13}$, 7,8-$C_2B_9H_{12}^-$, and $C_2B_{10}H_{13}^-$.[28] The hypothesis that fractional bonds are formed by localised molecular orbitals can apparently be also interpreted from the standpoint of delocalised three- and two-centre bonds, and they can be considered as delocalised (multicentre) bonds.

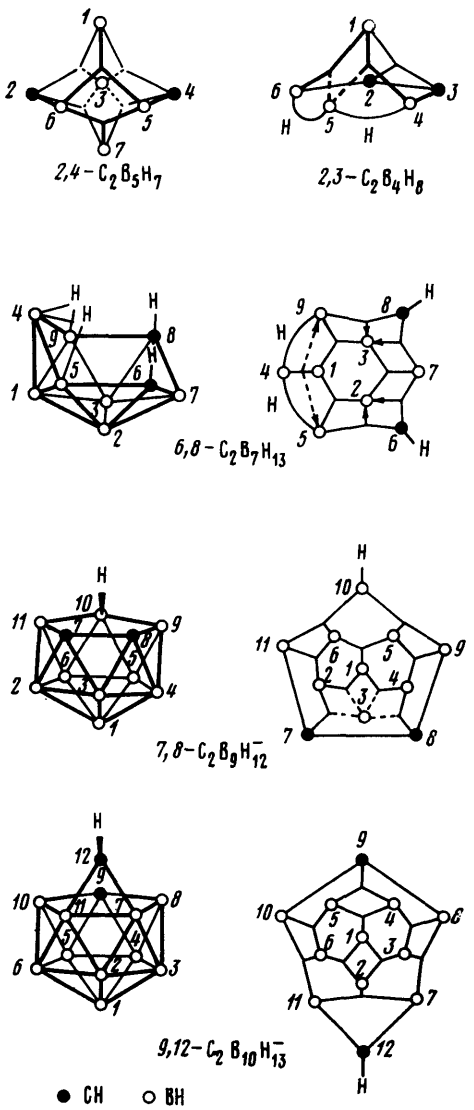


Figure 2. The valence structures of certain carbaboranes.

Since each valence line originating from an atom is usually associated with an atomic orbital, the notation used for fractional bonds requires some explanation. In this instance the "valence line" does not designate a localised atomic orbital but represents the direction of highest electron density in space. For localised two- and three-centre bonds, these concepts are identical. Within the framework of the valence bond method, fractional three-centre bonds can be described by resonance structures (Fig. 3).[41] The ideas concerning rapid electronic exchange processes and the combinatorial treatment of electron transfer in "electron deficient" polyhedral molecules have features in common with these concepts[45].

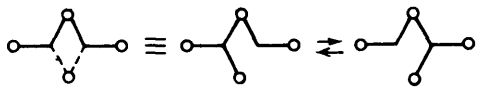


Figure 3. Representation of fractional three-centre bonds in terms of the valence bond method.

In polyhedral boron compounds localised two-centre bonds in general need not be normal σ bonds, since, owing to the geometrical characteristics of the molecular structure, they may not have axial symmetry, whereupon, like π bonds or "banana" type bonds, they should possess increased energy. This should in turn facilitate reactions with electrophiles involving such bonds and should lead to the formation of a three-centre bond (Fig. 4*a*).[2]

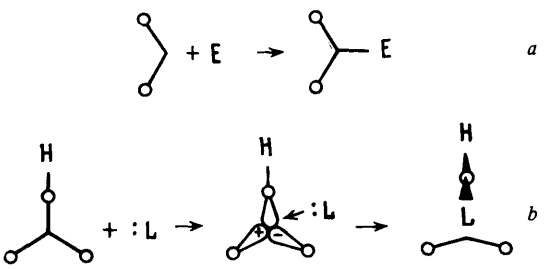


Figure 4. Models of the interaction of valence fragments of polyhedral boron compounds: *a*) formation of a two-centre bond with electrophiles; *b*) formation of a three-centre bond with nucleophiles.

Bonds of the second type, localised three-centre bonds, are characterised by three localised molecular orbitals, one of which is bonding and has low energy and the other two are antibonding. Depending on the symmetry and nature of the atoms forming the bond, one of the antibonding orbitals may have a very low position and its energy may approach that of a non-bonding level. Hence follows the high reactivity of the three-centre bond in relation to nucleophiles and reductants (Fig. 4*b*).[2]

Bonds of the third type in polyhedral compounds, delocalised (many-centre) bonds, are in general characterised by the presence of a high-energy HOMO and a low-energy LUMO. This should be manifested by a tendency of these bonds to undergo both electrophilic and nucleophilic reactions.

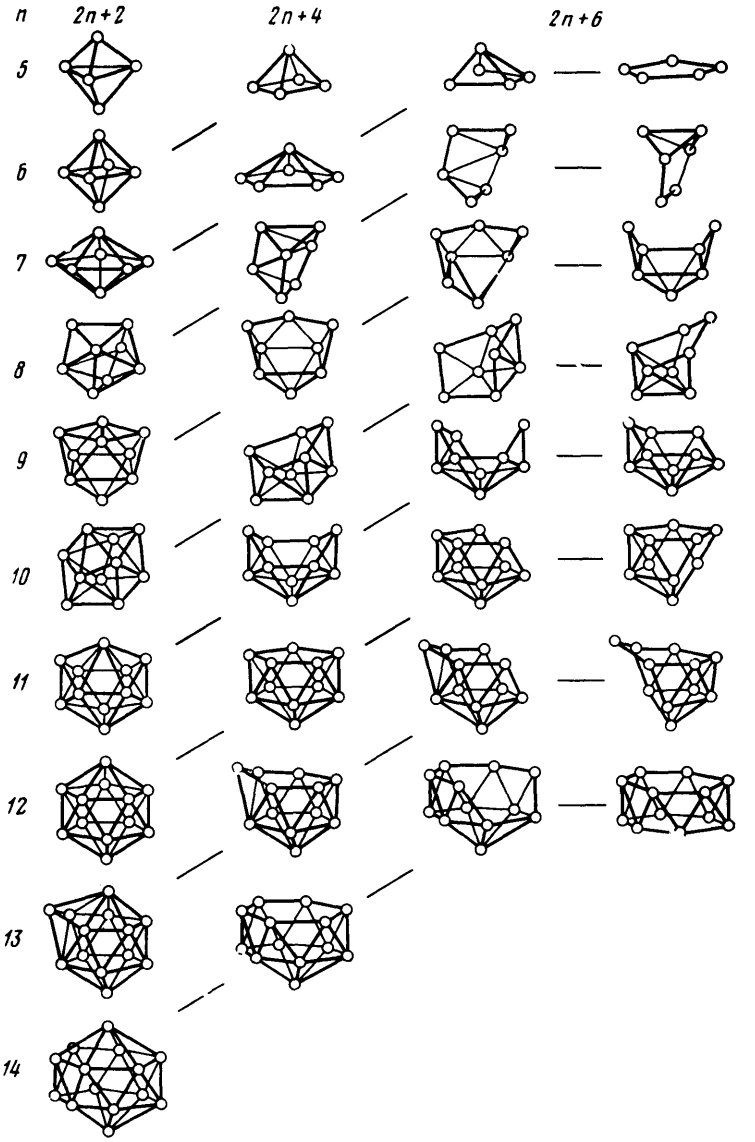


Figure 5. Relation between the type of structure of polyhedral boron compounds and their electronic structure (illustration of the Wade rule).

Thus chemical bonding in polyhedral boron compounds is characterised by a system of highly reactive two-, three-, and many-centre bonds. On the other hand, in the compounds under consideration there is no additional electronic system strongly binding the atoms of the molecular skeleton, in contrast to classical organic, particularly aromatic compounds where there exists, in terms of the σ–π approximation, a relatively inactive σ-skeleton imparting stability to the molecule in many reactions, in addition to the active π-electron system. Structural rearrangements of the molecular skeleton can therefore occur in polyhedral boron compounds during chemical reactions and thermal or electronic (under the influence of radiation) excitation.

2. RELATION BETWEEN THE NUMBER OF ELECTRONS AND THE STRUCTURE OF POLYHEDRAL COMPOUNDS

The direction of the rearrangements and the nature of the compounds formed are determined by the electronic structure of the polyhedral molecules and ions. Wade's rule, which establishes the relation between the number of electrons (or the number of electron pairs) participating in the binding of the atoms in the molecular skeleton and the type of structure, plays an important role in the understanding of the reductive and oxidative rearrangements of carbaboranes and other polyhedral boron compounds [13]. Rudolph and Pretzer [46] examined this relation in detail and confirmed by molecular orbital calculation the validity of

this rule: in particular they found that, when $n = 5$ for a system of $2n + 2 = 12$ electrons, there is a potential energy minimum corresponding to the *closo*-structure—a trigonal bipyramid, for a system with a $2n + 4 = 14$ electrons the minimum corresponds to the *nido*-structure—a tetragonal pyramid, and for a system with $2n + 6 = 16$ electrons, the minimum corresponds to the *arachno*-structure—a pentagonal fragment of a pentagonal bipyramid (Fig. 5). The authors[46] give an excellent illustration of this rule for the structural relation governing various polyhedral compounds[47]. This scheme (see Fig. 5) was supplemented by the present authors by the structures of closed polyhedra with 13 and 14 vertices and their fragments as well as certain alternative structures of *arachno*-compounds corresponding to the structures of borane and carbaborane ligands in transition metal complexes and, when $n = 9$, to the structure of the *arachno*-carbaborane $C_2B_7H_{13}$ (the first column in Fig. 5). This scheme does not include certain derivatives of boron hydrides and metalloboranes where bonds are formally formed by $2n$ electrons, for example in B_4Cl_4 (tetrahedron)[48-50], B_8Cl_8 (square antiprism)[51-54], B_9Cl_8H or $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$,[56] and $(\eta^5\text{-}C_5H_5)_3Co_3B_5H_5$.[57] As a possible structure of the above metalloboranes, Miller and Grimes[56] and Hall et al.[57] proposed $n - 1$ *closo*-polyhedra, where the "superfluous" BH or $Co(\eta^5\text{-}C_5H_5)$ structural unit is located above one of the triangular faces.

Among polyhedral boron compounds, there are examples of compounds which do not formally fit within the framework of the relations noted by Wade. We shall consider for example, the *arachno*-carbaboranes $C_2B_7H_{13}$[58,59] and $C_2B_8H_{14}$.[60,61] In these compounds the number of electrons binding the atoms of the molecular skeleton is the same as in the *closo*-carbaboranes $C_2B_7H_9$ and $C_2B_8H_{10}$ respectively. However, in the latter all the $3n$ atomic orbitals are involved in the construction of the molecular orbitals of the skeleton, while in *arachno*-carbaboranes only $3n - 2$ orbitals are involved, since two atomic orbitals, one from each carbon atom, form the C–H σ bond and for this reason there are two CH_2 structural units. Similarly in the series of the *nido*-carbaboranes $C_2B_7H_{11}$ has the BH_2 structural unit[62], i.e. $3n - 1$ atomic orbitals participate in the formation of the bonds of the skeleton; although the number of electrons binding the atoms of the skeleton is $2n + 2$, i.e. corresponds to the *closo*-structure, the compound is a *nido*-carbaborane and has an open structure.

Thus, when Wade's rule is applied to molecules in the ground state, account must be taken not only of the number of electrons binding the atoms in the skeleton but also of the total number of electrons in the $3n$-atomic orbitals of the n-atomic polyhedral molecule‡. In the more general case, including the excited states of the molecule, it is necessary to consider the number of occupied molecular orbitals made up of $3n$-atomic orbitals and not the number of electrons: the $n + 1$, $n + 2$, and $n + 3$ occupied orbitals will characterise the *closo*-, *nido*-, and *arachno*-structures respectively.

‡ $3n$ atomic orbitals are considered, and not the total number $4n$, because one orbital of each atom is involved in the formation of an outer σ bond and does not affect the nature of the structure.

3. REARRANGEMENTS INITIATED BY ELECTROPHILES AND NUCLEOPHILES

A graphical representation of localised two- and three-centre bonds can be conveniently employed for a clear description of reactions of polyhedral boron compounds with electrophiles and nucleophiles[2]. As already mentioned, chemical reactions with electrophiles E can proceed via two-centre or many-centre bonds (Figs. 4*a* and 6). In the latter case the reaction should lead to the localisation of the electron pair and the formation of either a three-centre bond BEB or a two-centre bond B–E or C–E with the electrophile. The reaction via a two-centre bond involves the intermediate formation of a three-centre bond BEB[2]. The strength of the latter is determined by the nature of the electrophile, the possibility of additional stabilisation as a result of the overlap of the electrophile orbitals, not involved in the formation of the bond, with the orbitals of the molecular skeleton, and finally, the symmetry of the three-centre bond[63,64]. Three-centre bonds BHB are quite stable. BEB bonds, where E = SiR_3, GeR_3, etc, are less stable and isomerise on heating in such a way that the electrophile moves to the terminal position relative to the boron atom (a B–E σ bond is formed), although the corresponding compounds with a bridge position of the electrophile E may be isolated and characterised, for example, μ-Me_3Si-2,3-$C_2B_4H_7$.[65-68] When E = Alk, compounds with a bridging alkyl group, for example μ-Alk-7,9-$C_2B_9H_{11}^-$ are stable only below 0°C, isomerising at room temperature to 10-Alk-7,9-$C_2B_9H_{11}^-$ in a few minutes[63,64]. Analogous compounds with an asymmetric alkyl bridge group, for example, in the 7,8-isomer (μ-Alk-7,8-$C_2B_9H_{11}^-$) are unstable even at low temperatures if they are formed at all.[12,69]

If the boron atoms forming a three-centre bond with the electrophile are non-equivalent, the BEB bond should be polarised in the direction ensuring the compensation of this non-equivalence. As a result of this, the three-centre bond is cleaved in such a way that the electrophile appears at the boron atom with the higher positive charge (in the initial state) (Fig. 6*a*). The directing effect in the rearrangement of the three-centre bond is static and to some extent resembles that in the directing effect in addition to the double bond in olefins.

There are several pathways leading to the transformation of a compound with a bridge group (Fig. 6). Pathways *b* and *c* (Fig. 6)§, leading to the formation of substitution products, were discussed in our earlier communication[2]. Pathways *d*, *e*, and *f* correspond to the oxidation of the system, i.e. to the closure of the polyhedron in the case of *nido*-compounds. Pathway *g* involves a rearrangement of the system, consisting in the migration of the boron atom with the substituent to the site of the missing vertex of the polyhedron with formation of a new isomer of the *nido*-carbaborane. As a result, the substituent passes to the terminal position and the hydrogen atom, previously in the terminal position, migrates to the bridge position. This mode of reaction was observed in the interaction of dicarbollide ions $C_2B_9H_{11}^{2-}$ with alkyl halides[12,63]. The driving force of this rearrangement is apparently electron transfer from the bonding orbital of the skeleton (B–Alk–B) to the B–Alkσ bond, oriented axially, i.e. involves in

§ Pathway *b* is in principle unlikely, since it requires the abstraction of a hydride hydrogen atom in the form of a proton.

essence the oxidation of the system and, in conformity with the Wade rule, the closure of the molecule into an octadecahedron. There are two σ-linked groups at the migrating boron atom in the transition state and stabilisation takes place as a result of further migration of the atom and the supply of electrons from the B–H σ bond to the bonding BHB orbital of the molecular skeleton. The molecule is then again opened and a fragment of an icosahedron with an equatorial orientation of the substituent is formed (Fig. 7).[12] The transition state in the given rearrangement can be stabilised, in principle, also as a result of the ejection of H^- or E^- (Alk^-) (Figs. 6*d*, 6*e*, and 6*f*) and in this instance the structure of the closed polyhedron is fixed (see also Section V, subsection 2).

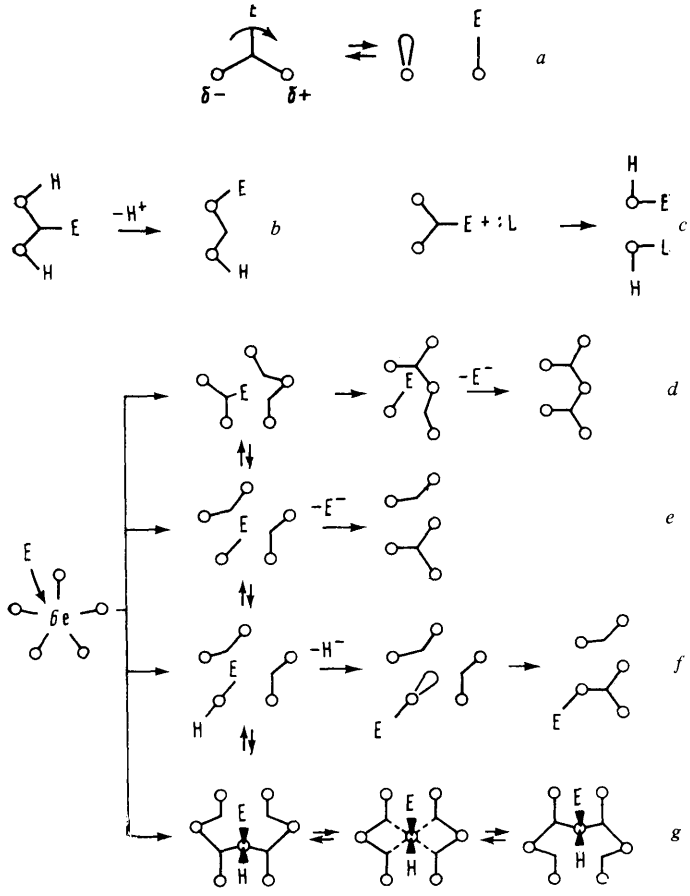


Figure 6. Possible rearrangements of bonds in systems with three- and many-centre bonds on interaction of two- and many-centre (five-centre) bonds with electrophiles.

The interaction of carbaboranes and other polyhedral compounds of boron with nucleophiles L and the reductants among them should proceed, as mentioned above, via three-centre and many-centre bonds having in the general case the lowest vacant orbitals. The attack by the nucleophile is on the three-centre bond and leads to its dissociation in such a way that L is oriented axially and H equatorially relative to the open face produced (Fig. 4*b*)¶. The stabilisation of the system requires the supply of electrons to orbitals linking the atoms of the molecular skeleton. This condition is fulfilled either on ejection of a proton from the boron atom forming a bond with the nucleophile and the involvement of the liberated electron pair in the binding of the atoms of the skeleton or after a rearrangement similar to that discussed above for the reaction of dicarbollide ions with alkyl halides. As a result electrons of the B–H σ bond (L) are used for the binding of the atoms of the skeleton, i.e. a BHB bridge bond is formed.

The characteristics found for the rearrangements initiated by electrophiles and nucleophiles show that, like the oxidative and reductive rearrangements, they proceed with a change in the number of electrons and in the general case in the number of orbitals binding the atoms of the skeleton of the molecule or ion in the transition state. We suggest that the thermal rearrangements of closed polyhedral systems can also proceed via a transition state in which the number of orbitals occupied by electrons changes (increases). As will be shown below, this is equivalent to the supply of additional electrons to the vacant orbitals. Thus, in the course of such thermal rearrangements, one may expect the opening of the *closo*-structure to the *nido*-structure due to electron transfer to a vacant orbital closest as regards energy and subsequent reclosure of the polyhedron, but in another direction. The foregoing permits the conclusion that an essential condition for the above rearrangements is a change in the number of occupied molecular orbitals during the reaction.

III. QUANTUM-CHEMICAL CRITERIA OF THE REARRANGEMENTS

The quantum-chemical approach is the most general and promising when the rearrangements of polyhedral molecules are considered. The possibility of determining the potential energy surface for a given system enables one to characterise unambiguously and quantitatively all possible molecular transformations. The difficulty of calculations of this kind in practice suggests that it might be useful to determine semiquantitative or even qualitative but objective criteria characterising a given rearrangement. The prediction of the relative configurational stability, direction, and mechanism of the rearrangements can be based in many instances on the first- and second-order Jahn–Teller effects[70]. The first-order Jahn–Teller effect arises under the following conditions: when a molecule with a given symmetry has a degenerate electronic state, the corresponding configuration of atoms in the polyhedral molecule is unstable and the structure changes in such a way that the degeneracy is removed[71]. Rearrangements of the skeleton can be both static and dynamic, i.e. the degeneracy may be removed by the vibrational motions of the molecule. The second-order Jahn–Teller effect is manifested when there is no degeneracy in the ground state but the boundary molecular orbitals have similar energies[70]. In this case the symmetry

¶When the nucleophile approaches from the other side of the bond (from the side opposite to the direction of the corresponding atomic orbital), L and H have the opposite orientations: equatorial for L and axial for H.

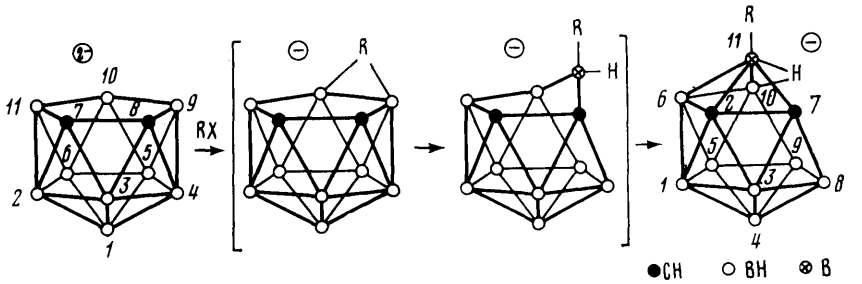


Figure 7. The proposed mechanism for the rearrangement of 7,8-dicarba-*nido*-undecaborate to the 2,7-isomer during the reaction of the dicarbollide ion with alkyl halides.

of the HOMO and LUMO and the energy gap between them determines the possibility of the rearrangement (makes it symmetry-allowed) and its ease in the particular direction.

It has been shown[72-74] that the energy change in the system following a small shift along a normal coordinate Q can be represented as follows:

$$E_0 - E_0' = \Delta E_0 = Q\left\langle \Psi_0 \left| \frac{\partial V}{\partial Q} \right| \Psi_0 \right\rangle + \frac{1}{2} Q^2 \left\langle \Psi_0 \left| \frac{\partial^2 V}{\partial Q^2} \right| \Psi_0 \right\rangle + Q^2 \sum_k \frac{\left[\left\langle \Psi_0 \left| \frac{\partial V}{\partial Q} \right| \Psi_k \right\rangle\right]^2}{E_0 - E_k}; \quad (1)$$

having assumed that the first term of the series characterising symmetrical shifts is zero, i.e. by considering only shifts which alter the initial molecular symmetry, the following expression was obtained[74]:

$$\Delta E_0 = \frac{1}{2} Q^2 \left\langle \Psi_0 \left| \frac{\partial^2 V}{\partial Q^2} \right| \Psi_0 \right\rangle + Q^2 \sum_k \frac{\left[\left\langle \Psi_0 \left| \frac{\partial V}{\partial Q} \right| \Psi_k \right\rangle\right]^2}{E_0 - E_k} = f_{00} Q^2 + f_{0k} Q^2, \quad (2)$$

where Ψ_0 and Ψ_k are the wave functions of the ground degenerate state with the energy E_0 and of the excited state with the energy E_k and V is the potential energy of the system corresponding to the nucleus–nucleus and nucleus–electrons interactions.

For any Q, we have $f_{00} > 0$, since it characterises the energy change averaged with respect to the initial optimised electron distribution. On the other hand, $f_{0k} < 0$, since $E_0 - E_k < 0$. Thus the stability of the given molecular configuration in relation to the rearrangement along the coordinate Q is determined by the relative values of f_{00} and f_{0k}:

(1) $f_{00} \gg f_{0k}$, $\Delta E_0 \gg 0$—system with the given symmetry is stable;

(2) $f_{00} \sim f_{0k}$, $\Delta E_0 \sim 0$—a rearrangement with a low activation energy is possible;

(3) $f_{00} \ll f_{0k}$, $\Delta E_0 \ll 0$—system is unstable and rearranges spontaneously to a system with another symmetry[74].

In a qualitative consideration of rearrangements it is not necessary to consider all the excited states and the treatment may be restricted to the one-electron transition between occupied and unoccupied boundary orbitals. These transitions can be observed experimentally in the ultraviolet and visible spectra. The smaller the energy gap and the closer the HOMO and LUMO levels, the greater the ease of the rearrangement. The initial configuration is regarded as unstable if the energy gap is < 4 eV.[74]

The choice of the possible direction of the rearrangements is restricted to the condition where the integral $\langle \Psi_0 | \partial V/\partial Q | \Psi_k \rangle$, which is included in the expression for f_{0k}, is not equal to zero. For this purpose, the representations of the given coordinate Q should be included in the products of the representations of the boundary molecular orbitals, and in the more general case of the orbital ψ_i, occupied in Ψ_0, and the orbital ψ_j, populated in Ψ_k.[74]

The Jahn–Teller effects can have important stereochemical manifestations in the chemistry of polyhedral boron compounds and can be used both for the explanation of the existing empirical rules, for example the Wade rule, and for the prediction of the possible mechanisms of the rearrangements of the skeleton of a polyhedral molecule[63].

It is possible to distinguish the following most characteristic manifestations of these effects.

1. The thermodynamic and kinetic stabilities of polyhedral boron compounds in relation to thermal rearrangements are determined by the energy gap ΔE between the boundary molecular orbitals, which, as already mentioned, may be estimated from spectroscopic data. For example, in the case of icosahedral carbaboranes(12) ΔE is large, which follows from the absence of absorption in the visible and ultraviolet spectra up to 200 nm, i.e. $\Delta E > 6$ eV, and the rearrangements of $C_2B_{10}H_{12}$ are observed only at temperatures of approximately 500°C and above. On the other hand, the spectra of the monoanions $C_2B_{10}H_{13}^-$ show absorption bands with a maximum at $\lambda = 260$ nm[75] and $\Delta E = 4.8$ eV; as a result of this, the rearrangements in the monoanions occur even at 100°C.[76,77] The dianions $C_2B_{10}H_{12}^{2-}$ derived from 1,2- and 1,7-$C_2B_{10}H_{12}$ absorb at $\lambda = 300$ nm, and those derived from 1,12-$C_2B_{10}H_{12}$ absorb at 335 nm,[75] to which correspond $\Delta E = 4.1$ and 3.7 eV respectively, and the rearrangements proceed readily at room temperature. The possible direction and type of the resulting isomers are then determined by other factors, including the symmetry of the boundary molecular orbitals.

When the mechanisms of thermal rearrangements are considered, it is striking that deformations which do not alter the initial molecular symmetry should be excluded from consideration. Otherwise, the first term of the expansion, which is positive by definition, must be again taken into account in Eqn. (1). Furthermore, the representation of a fully symmetrical deformation can be included only in the product of the deformations of boundary orbitals with identical symmetry. Thus fully symmetrical deformations will increase greatly the energy of the system. For example, in the rearrangements of icosahedral

carbaboranes $C_2B_{10}H_{12}$ the mechanisms involving a cubo-octahedral transition state appear unlikely on symmetry grounds, since the corresponding normal vibrations of a molecule with C_{2v} symmetry are fully symmetrical (see also Section V, subsection 2).

2. Any change in the number of orbitals occupied by electrons should lead to the destabilisation of the molecules or ions having a given symmetry. Indeed the atoms of the skeleton tend to assume a configuration such that all the electrons occupy bonding orbitals and the energy gap ΔE between the boundary orbitals is a maximum. For example, although the addition of electrons reduces the energy of the system on the whole, it destabilises the molecule or ion with the given symmetry relative to the zero non-bonding level, since the electrons are accommodated in antibonding molecular orbitals. The ease of rearrangements leading to a change in the initial symmetry and the accommodation of additional electrons at a bonding level is determined by the low value of ΔE between the antibonding orbital being filled and the nearest unfilled orbital and the occurrence of normal vibrational displacements with a suitable symmetry. In the borane anions $B_nH_n^{2-}$ ($n = 5,6,7,8,10,12$), the LUMO are degenerate[14,18], so that the rearrangements arising on increasing the number of electrons and the formation of $B_nH_n^{4-}$ may be caused by the first-order Jahn–Teller effect[46]. On passing the corresponding carbaboranes, for example, the $C_2B_nH_{n+2}$ series, the symmetry of the polyhedral molecule decreases, for example, from I_h in $B_{12}H_{12}^{2-}$ to C_{2v} in 1,2- and 1,7-$C_2B_{10}H_{12}$ or D_{5d} in 1,12-$C_2B_{10}H_{12}$. This should be accompanied by the splitting of the corresponding degenerate levels. However, the splitting is apparently not very great and the addition of electrons to carbaboranes and heteroboranes is also accompanied by a change in the initial structure owing to the second-order Jahn–Teller effect†. Here one should note that the degeneracy of the ground state is not in the general case a sufficient condition for the rearrangements (static deformations), as has been suggested, for example, by Rudolph and Pretzer[46] and Pearson[74]. In most cases the electronic degeneracy is converted into a vibronic degeneracy as a result of dynamic processes (see Bersuker[78], chapter VI). However, owing to the specific features of the reactions with nucleophiles and reductants via three-centre or many-centre bonds in polyhedral boron compounds, the addition of electrons should lead to the opening of the closed polyhedral molecule with formation of a tetragonal, pentagonal, or hexagonal face[2] (see also Sections II and IV).

3. The excitation of an electron to a vacant orbital is equivalent in terms of its stereochemical consequences to the addition of one or two electrons to the same orbital, and the symmetry of the molecule in the excited state should therefore be the same as that of the molecule which has combined with one or two electrons[79]. Thus, on excitation of electrons, there is a possibility of easy rearrangements of the atoms of the skeleton and the consequent formation of, for example, positional isomers depending on the positions of the substituents and heteroatoms in the polyhedral molecule. When the stereochemical results of the excitation or addition of electrons to a polyhedral molecule are compared, account must be taken of the lifetime of the excited state of the molecule. If the latter is short, the system may not attain the optimum configuration and the structure of the excited molecule may differ from that which has combined with the electrons.

4. The change in the symmetry of the polyhedral molecule or ion when the number of occupied orbitals is altered is determined by the symmetry of the possible soft deformations, i.e. the deformations of the boundary molecular orbitals. After the rearrangement, a molecule (ion), characterised by the correspondence of the number of occupied bonding orbitals with the number of electrons and by the maximum energy gap, is formed.

5. The decrease of molecular symmetry, i.e. the symmetry of the molecular orbitals, after the introduction of polar substituents at the atoms of the skeleton of the polyhedral molecule should lead, as already mentioned, to the splitting of the molecular orbital energy levels. Consequently, in the general case there is a possibility of the mutual approach of the HOMO and LUMO levels. In conformity with the second-order Jahn–Teller effect, this is manifested by the facilitation of the rearrangements of the corresponding molecules and by an increase of their reactivity. For example, the introduction of polar substituents in 1,5-$C_2B_3H_5$ destabilises the molecule to such an extent that the compounds prove to be unstable at room temperature[80].

The fundamental principles and rules of both thermal and reductive and oxidative rearrangements follow from the data discussed above: the Wade rule for rearrangements induced by a change in the number of electrons in the system, and the change in the number of molecular orbitals, binding the atoms of the molecular skeleton and occupied by electrons in the ground and transition states, for a series of thermal rearrangements.

IV. REDUCTIVE AND OXIDATIVE REARRANGEMENTS

According to the Wade rule, any change in the number of electrons without the alteration of the given set of molecular orbitals in conformity with the Jahn–Teller effects, should be accompanied by the destabilisation of the initial configuration and a change in the symmetry of the skeleton of the molecule or ion. When electrons are added, the molecule tends to undergo a rearrangement to achieve an increase in the number of bonding orbitals, and when electrons are removed, it tends to undergo a rearrangement involving a corresponding decrease. The Wade rule fully satisfies these requirements. For example, the addition of two electrons to an n-atomic polyhedral molecule with a *closo*-structure, i.e. having $n + 1$ electron pairs and the corresponding number of bonding orbitals, should lead to a *nido*-structure of the n-atomic fragment of an $(n + 1)$-atomic closed polyhedron having $n + 2$ pairs of bonding electrons distributed in $n + 2$ bonding orbitals.

1. REDUCTIVE REARRANGEMENTS

(a) The Addition of Electrons

The three-centre bonds between carbon and boron atoms in *closo*-carboaranes are the most polarised and therefore have the lowest unoccupied molecular orbitals. This determines the course of the reactions with nucleophiles, including reductants, formally at the boron atoms adjoining carbon atoms. The opening of a *closo*-structure to give a *nido*-structure after the addition of two electrons with formation of a pentagonal or hexagonal face may be

† If the LUMO remain degenerate in the given compounds, the rearrangement is again determined by the first-order Jahn–Teller effect.

accounted for by the rearrangement of the three-centre bonds to two-centre bonds in accordance with the schemes illustrated in Fig. 8.[2] The reduction is usually carried out with metallic sodium in liquid ammonia or tetrahydrofuran (THF). In the latter case electron-transferring agents, for example, naphthalene, are frequently used to achieve the addition of two electrons[81,82]. Electrochemical reduction of polyhedral molecules has also been described[83-87].

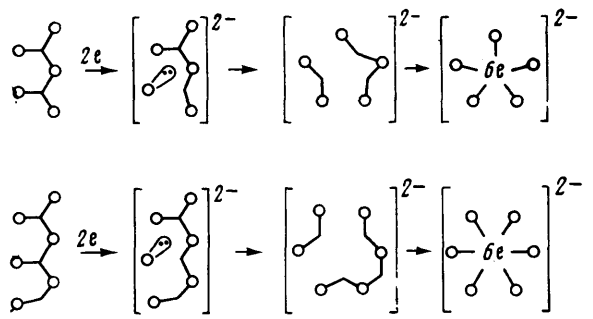


Figure 8. Models of the interaction of possible fragments of polyhedral molecules with reducing agents.

The complexity of the study of reactions involving the addition of electrons to polyhedral molecules consists in the fact that, owing to the one-electron multistage mechanism of this process, radical-anions are formed at an intermediate stage and this determines in many instances the course of cross-linking and disproportionation reactions. Furthermore, the dianions formed may not be individual species and may consist of sets of dynamic structures. Thus the energy barriers between different $C_2B_3H_5^{2-}$ isomers are very low and easy rearrangements of the atoms of the skeleton are therefore possible[10]. The interaction of the dianions with electrophiles is accompanied by the fixation of the open structure and it is possible to isolate individual compounds. Protonation of the dianions leads to the corresponding monoanions and uncharged *nido*-carbaboranes. Depending on the nature of the binding of the proton, the open face retains its structure completely on formation of the BHB bridge bond or partly contracts on formation of B–H or C–H bonds[2]. The above features are illustrated by the examples described below.

$1,2\text{-}C_2B_8H_{10}$. The addition of two electrons to $1,2\text{-}C_2B_8H_{10}$ gives rise to a dianion whose protonation gave the *nido*-carbaborane $5,6\text{-}C_2B_8H_{12}$ (Fig. 9) in 30% yield[88]. The reduction of *nido*-$5,6\text{-}C_2B_8H_{12}$ with sodium amalgam in ethanol leads, in conformity with the Wade rule, to the *arachno*-carbaborane $6,9\text{-}C_2B_8H_{14}$ in 26% yield. The formation of the 6,9-isomer in this reaction can be explained by the migration of the $C_{(6)}$ atom (Fig. 9).[61]

$C_2B_{10}H_{12}$. The dianions of all the carbaborane(12) isomers and many of their *C*- and *B*-derivatives have now been investigated. The results of the early theoretical calculations suggested that the addition of electrons to $C_2B_{10}H_{12}$ may not be accompanied by a significant change in the icosahedral structure[14,34]. It was therefore postulated that the opening of the icosahedral molecule does not occur in the stage involving the addition of electrons to the molecule, but during the protonation of the dianions formed[14]. However, experimental ^{11}B NMR, infrared spectroscopic, and ultraviolet spectroscopic data indicate a significant change in the icosahedral structure of $C_2B_{10}H_{12}$ molecules when electrons are added to them. The ^{11}B NMR spectra of the dianions derived from *o*-, *m*- and *p*-$C_2B_{10}H_{12}$ and their various derivatives, recorded at 32.1 MHz by a double resonance technique, are characterised by a set of broad lines over a wide frequency range and differ fundamentally from the spectra of the initial carbaboranes(12)[75,89]. The *nido*-structure of $C_2B_{10}H_{12}^{2-}$ is also indicated by the infrared spectra of the dianions in THF solution where there are two signals in the range 2400–2600 cm^{-1} due to the stretching vibrations of two types of B–H bonds, apparently located in the open face and in the closed part of the polyhedron. The ultraviolet spectra of the dianions $C_2B_{10}H_{12}^{2-}$ derived from 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ contain absorption bands with maxima at 298 ± 10, 295 ± 10, and 335 nm respectively. This distinguishes them from the initial icosahedral carbaboranes, which do not absorb in the visible and ultraviolet (up to 200 nm) spectra[75].

On the basis of these data, we suggest that the dianions $C_2B_{10}H_{12}^{2-}$ have a structure of the molecular skeleton similar to that of the corresponding carbaborane ligands in transition metal complexes (Fig. 10) and are characterised by rapid dynamic rearrangements of the molecular skeleton[75,89].

The chemical properties of the dianions derived from 1,2- and $1,7\text{-}C_2B_{10}H_{12}$ indicate specific differences between their structures. Thus protonation of these dianions under identical conditions gives rise to mixtures differing in the ratio of the isomeric monoanions[75,89]. Oxidation of the complexes of the corresponding dianions by cobalt(III) also leads to neutral carbaboranes(12) with different yields and different mixture compositions[89,90]. The nature of the

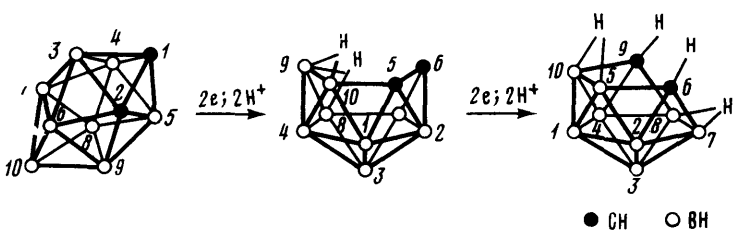


Figure 9. The opening of *closo*-$1,2\text{-}C_2B_8H_{10}$ to give *nido*-$5,6\text{-}C_2B_8H_{12}$ and *arachno*-$6,9\text{-}C_2B_8H_{14}$ on reduction and subsequent protonation.

structural differences between the dianions cannot be determined exactly by experimental methods. Presumably they are associated with the different positions of carbon atoms in the open face: for example, 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ give rise to the dianions 7,9-$C_2B_{10}H_{12}^{2-}$ and 7,10-$C_2B_{10}H_{12}^{2-}$ respectively. The structure in which only one carbon atom is on the open face has been suggested for the dianion derived from 1,12-$C_2B_{10}H_{12}$ (Fig. 10).[11]

It is noteworthy that the dianions obtained from 1,2- and 1,7-$C_2B_{10}H_{12}$ have similar spectroscopic characteristics. Furthermore, oxidation of these dianions leads to the same product—1,2-$C_2B_{10}H_{12}$. Some workers used these data as the basis for the hypothesis that the dianions from 1,2- and 1,7-$C_2B_{10}H_{12}$ are identical[77,83,91,92]. However, the foregoing considerations, the non-characteristic nature of the spectroscopic characteristics examined, and the possibility of the formation of *o*-carbaborane(12) on closure of the fragment of a 13-vertex polyhedron with an arbitrary distribution of carbon atoms in the open face[11,75] led us to the conclusion that this view is erroneous.

(b) Electrochemical Reduction

$C_2B_9H_{11}$. The electrochemical reduction of *closo*-2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$ and its *B*-hydroxy- and *B*-alkoxy-derivatives proceeds in stages. The first stage leads to the formation of radical-anions. For 2,3-$(CH_3)_2$-$C_2B_9H_9$ and its *B*-hydroxy-derivatives, this process is electrochemically irreversible, which is attributed to the possibility of the occurrence of a chemical reaction or a change in the carbaborane molecule. For B-alkoxy-derivatives of carbaborane(11), the addition of two electrons in stages is observed, the first stage being reversible. The radical-anions formed are stable in this case. Analogous stable radical-anions are formed when the corresponding carbaboranes are acted upon by sodium in THF. Both electrochemical and chemical (Na in THF) addition of an electron to the radical-anions leads to the formation of derivatives of 7,9-$C_2B_9H_{11}^{2-}$ dianions[87].

$C_2B_{10}H_{12}$. In contrast to the multistage reduction of $C_2B_9H_{11}$ derivatives discussed above, a single two-electron wave is observed in the electrochemical reduction of icosahedral *o*-carbaboranes[83-86].

(c) Transition Metal Complexes of the Dianions

The fixation of the structure of the dianion and the overall stabilisation of the carbaborane ligand take place also when transition metal complexes are formed. The addition of electrons from sodium to polyhedral molecules with a *closo*-structure and subsequent treatment with transition metal salts and $C_5H_5^-Na^+$ constitute one of the main methods for the synthesis of metallocarbaboranes, metalloheteroboranes, and metalloboranes (the polyhedral expansion method[81,82,93-97]). The method involving the direct insertion of a transition metal atom in the polyhedral molecule without preliminary reduction of the latter[98-102] is in essence analogous to the polyhedral expansion method, since in this case electrons are also transferred to the polyhedral molecule, but this time from the transition metal atom‡ and the reduction and complex formation stages are thus combined. Since the number of atoms constituting the molecular skeleton changes in these reactions (increases), we shall describe only the fundamental principles without considering in detail all the available literature data concerning the synthesis of metal-containing molecules and ions (see the relevant reviews[103-106]). The rearrangements of polyhedral molecules in polyhedral expansion reactions are fully consistent with the Wade rule, i.e. complexes having the structure of the next polyhedron are formed as a result. The metal atom then occupies the vertex with the highest coordination number. As a result of the addition of electrons, the initial polyhedral molecule rearranges and becomes a ligand in the complex. The structure of the ligand corresponds to the structure of a fragment of the next polyhedron (the Wade rule) and in carbaborane ligands the carbon atoms are located in the open face. This reflects the mode of addition of electrons

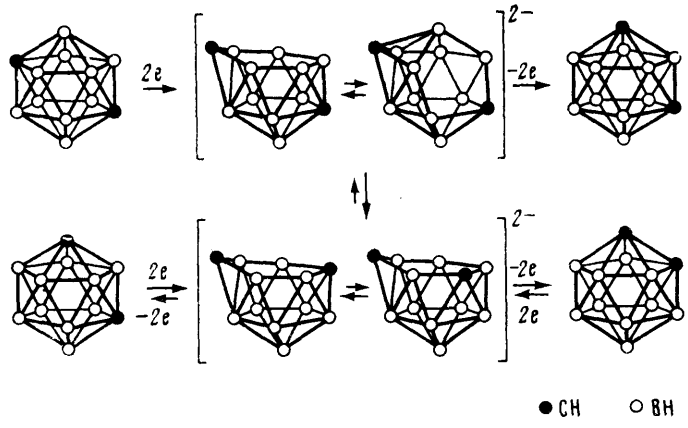


Figure 10. The possible modes of opening of icosahedral carbaboranes following the addition of electrons and rearrangement of the resulting dianions.

‡ For example, the following transition metal complexes are used as reagents: $Fe(CO)_5$, $(C_5H_5)Co(CO)_2$, $(C_2H_4)Ni(PPh_3)_2$, (*trans*-stilbene)$Pt(PMe_3)_2$, etc.

and the stability of the corresponding dianions in which the carbon atoms are in the open face.

Successive application of the polyhedral expansion method yielded metallocarbaboranes containing two and three transition metal atoms, i.e. formally the initial n-atomic molecule with a *closo*-structure, which ultimately combines with three pairs of electrons, is converted into an n-atomic fragment of the $(n + 3)$-atomic polyhedron and the sites of the three missing vertices are occupied by the transition metal atoms (Fig. 11*a*). The hitherto unknown structures of polyhedra with 13 and 14 vertices were also obtained by the polyhedral expansion reaction of the icosahedral carbaborane (Figs. 11*b* and 11*c* [95]).

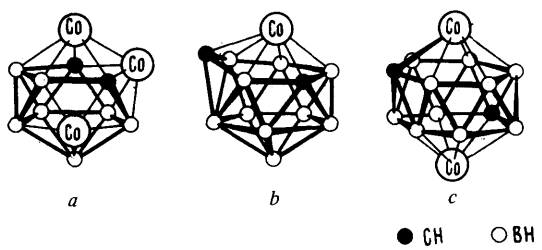


Figure 11. The structures of metallocarbaboranes obtained by the polyhedral expansion method: *a*) 1,2,8,3,6-(η^5-C_5H_5)$_3$$Co_3C_2B_7H_9$; *b*) 1,2,4-($\eta^5$-$C_5H_5$)$CoC_2B_{10}H_{12}$; *c*) 1,14,2,10-($\eta^5$-$C_5H_5$)$_2$$Co_2C_2B_{10}H_{12}$ (suggested structure of one of the isomers). The ligands C_5H_5 are not shown in the Figure.

By reducing the carbaboranes $Me_4C_4B_8H_8$ with $NaC_{10}H_8$ and subsequent treatment with NaC_5H_5 and $FeCl_2$, Grimes and coworkers [97] obtained several (η^5-C_5H_5)$_2$$Fe_2Me_4C_4B_8H_8$ isomers. X-Ray diffraction analysis established that two out of the four isomers isolated have the structure of 14-vertex fragments of 15-vertex closed polyhedra with an open tetragonal or pentagonal face [the *nido*-structure of a $(2n + 4)$-electron polyhedron] (Fig. 12). Nevertheless, the authors [97] believe that 14 atoms of the molecular skeleton are linked by 30 electrons, i.e. belong to the type of $(2n + 2)$-electron polyhedra, which should have a *closo*-structure according to the Wade rule.

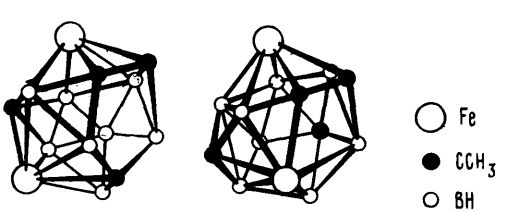


Figure 12. The structures of 15-vertex *nido*-metallocarbaboranes. The ligands C_5H_5 are not shown in the Figure.

Hawthorne and coworkers [107] examined the problem of the application of the Wade rule to metallocarbaboranes. Taking into account the tendency of the transition metal atom to complete its outer electron shell, i.e. to have 18 electrons in the latter, and also the fact that six ligand electrons participate in the coordination of the ligand to the transition metal, the "magic numbers" determining the type of structure and class of metallocarbaboranes were also derived. For complexes with a single transition metal atom and a single carbaborane ligand, $2n + 14$ electrons characterise *closo*-compounds and $2n + 16$ electrons characterise *nido*-compounds. For the metal : ligand = 1 : 2 ratio, the corresponding numbers are $2n + 12$ for a *closo*-structure, $2n + 14$ for *closo*- and *nido*-structures, and $2n + 16$ for a *nido*-structure. For the ratio 2 : 1, a polyhedral *closo*-molecule is characterised by $2n + 26$ electrons [107].

In his study of the structure of transition metal complexes with dicarbollide ions, Wegner [108] noted that the molecules have an icosahedral structure for metals with a $d^5 - d^7$ electronic configuration and a significantly distorted (open) structure for $d^8 - d^9$ metals. The transition from a d^6 configuration to d^7, d^8, and d^9 configurations is equivalent to the addition of one, two, and three electrons respectively. Thus the opening of an icosahedral *closo*-structure takes place directly in the reduction of the polyhedral system and not in the protonation stage [108].

(d) The Addition of Nucleophiles

Reductive rearrangements (opening) of closed polyhedral molecules as a result of the addition of nucleophiles should include, as already noted, several stages apart from the addition of electrons (see also the footnote in Section II, subsection 3): the ejection of a proton from the boron atom with which the nucleophile has formed a bond, and reorientation of the resulting atomic orbital with an electron pair; another more probable reaction pathway involves a rearrangement of the polyhedral molecule and the supply of electrons from the B–H bond to the orbitals of the skeleton as a result of the formation of a BHB bridge bond. If the compound formed is unstable, for example, because the carbon atoms are not located in the open face, stabilisation may be achieved due to further rearrangements (see Section V, subsection II).

$C_2B_4H_6$. The addition of nucleophiles, for example, Me_3N, Me_3P, or H^-, to *closo*-1,6-$C_2B_4H_6$ leads to the opening of the molecule and the formation of *nido*-5-Me_3N-2,4-$C_2B_4H_6$, 5-Me_3P-2,4-$C_2B_4H_6$, and 2,4-$C_2B_4H_7^-$ respectively (Fig. 13*a*). [109-111]

$C_2B_9H_{11}$. The interaction of 2,3-$C_2B_9H_{11}$ with a wide range of nucleophiles L proceeds with formation of 10-L-7,9-$C_2B_9H_{11}^-$ [112-114] (Fig. 13*b*). The suggested formation of 3-L-7,9-$C_2B_9H_{11}^-$ was disproved [115,116].

The opening of closed polyhedral metallocarbaboranes on treatment with nucleophiles has been observed in many instances [117-119].

2. OXIDATIVE REARRANGEMENTS

The oxidative rearrangements of *nido*-carbaboranes may be described in terms of schemes which are the opposite of those for the addition of electrons. The oxidant E interacts with the highest occupied two-centre or delocalised five- or six-centre orbital and a two-centre B–E or C–E bond or a three-centre BEB bond is formed. The opening of the latter and the formation of a B–E or C–E bond lead

to partial closure of the *nido*-structure. Electron transfer to the oxidant completes the closure of the structure (Figs. 6*d*, 6*e*, and 6*f*). Evidently the mode of oxidative rearrangements is determined by the direction of electrophilic attack and may not take place along the same coordinate as the reverse process involving the opening of the structure under the influence of a reductant or a nucleophile.

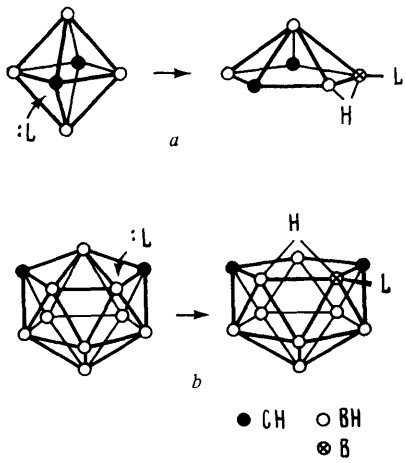


Figure 13. The opening of *closo*-carbaboranes on interaction with nucleophiles: *a*) 1,6-$C_2B_4H_6$; *b*) 2,3-$C_2B_9H_{11}$.

Many transformations of neutral *nido*-carbaboranes into *closo*-carbaboranes on pyrolysis may be classified as oxidative rearrangements. Such a reaction is used in the synthesis of all the lower and medium carbaboranes $C_2B_nH_{n+2}$:

$$C_2B_9H_{13} \xrightarrow{-H_2} C_2B_9H_{11}\ ^{58,\,120},$$
$$C_2B_8H_{12} \xrightarrow{-H_2} C_2B_8H_{10}\ ^{62,\,88,\,121-120},$$
$$C_2B_7H_{13} \xrightarrow{-H_2} C_2B_7H_9\ (+\ C_2B_6H_8 + C_2B_8H_{10})\ ^{58,\,124},$$
$$C_2B_4H_8 \xrightarrow{-H_2} C_2B_4H_6\ (+\ C_2B_3H_5 + C_2B_5H_7)\ ^{125-127}.$$

Owing to the radical mechanism of the pyrolysis, reactions involving the disproportionation or cross-linking of the polyhedral molecules frequently occur. Intramolecular oxidation (closure) also takes place when a halide anion is eliminated from (B)-Hal-$C_2B_{10}H_{11}^{2-}$ [128]:

$$(C_2H_{10}H_{11}X)^{2-} \rightarrow C_2B_{10}H_{11}^{-} + X^{-}.$$

Depending on the distribution of electron density in the open face of the polyhedral molecule, reactions with electrophiles can proceed in different ways and the oxidative rearrangement can lead to different products.

Examples of the oxidative rearrangements of open polyhedral compounds are the closure of thioboranes on oxidation and pyrolysis [129]:

$$arachno\text{-}6\text{-}SB_9H_{12}^{-} \xrightarrow{-2e,\,[O]} nido\text{-}6\text{-}SB_9H_{11} \xrightarrow{-H_2\,(t^\circ)} closo\text{-}1\text{-}SB_9H_9,$$

the formation of *closo*-2,3-$C_2B_9H_{11}$ on oxidation of *nido*-7,9-$C_2B_9H_{11}^{2-}$ with stannous chloride [114]:

$$nido\text{-}7,9\text{-}C_2B_9H_{11}^{2-} \xrightarrow{-2e\,(SnCl_4)} closo\text{-}2,3\text{-}C_2B_9H_{11},$$

and oxidative rearrangements of carbaborane(12) dianions and their derivatives.

A characteristic feature of the oxidative rearrangements of the dianions $C_2B_{10}H_{11}^{2-}$ is that they lead to isomers of the icosahedral carbaborane(12), which are in general different from the initial isomers. For example, the oxidation of the dianions of both 1,2- and 1,7-$C_2B_{10}H_{12}$ leads exclusively to 1,2-$C_2B_{10}H_{12}$, [83] while the dianion derived from 1,12-$C_2B_{10}H_{12}$ yields only 1,7-$C_2B_{10}H_{12}$. [130,131] The oxidation of the dianions derived from a series of *C*-derivatives of *p*-carbaborane yields also derivatives of the *o*-isomer together with those of the *m*-isomer, depending on the type and number of substituents [11,75,132,133]. The direction of the rearrangements is greatly influenced by substituents in the carbaborane ring. The oxidative rearrangement of the dianion obtained from 2-Hal-1,12-$C_2B_{10}H_{11}$ leads to a mixture of the two possible isomers of (B)-Hal-1,7-$C_2B_{10}H_{11}$ and unsubstituted 1,12- and 1,7-$C_2B_{10}H_{12}$. Mainly 10-Hal- and 3-NH_2-$C_2B_{10}H_{12}$ are formed together with 1,2- and 1,7-$C_2B_{10}H_{12}$ from 9-Hal-1,7-$C_2B_{10}H_{11}$ under analogous conditions [130]. In many instances the influence of the substituent is so great that the direction of the rearrangement changes; for example, derivatives of the 1,7-isomer are formed together with those of 1,2-$C_2B_{10}H_{12}$ in the oxidation of the dianion obtained from 1-CH_2Hal-1,2-$C_2B_{10}H_{11}$. [134]

Thus the set of experimental data shows that the substituent influences the direction not only of oxidative but also of reductive rearrangements and the occurrence of the rearrangements in the dianions themselves.

Oxidative rearrangements of *nido*-metallocarbaboranes lead to the closure of the polyhedron, as expected [135].

V. THERMAL REARRANGEMENTS

1. REARRANGEMENT OF CLOSED POLYHEDRAL SYSTEMS

The rearrangements of closed polyhedral molecules take place over a wide temperature range. For example, the anions $B_2H_6^{2-}$, $B_{11}H_{11}^{2-}$, and $CB_{11}H_{11}^{-}$ rearrange so fast that the characteristics of the ^{11}B NMR spectra of these species in solution at room temperature and below are averaged out. On the other hand, 1,7-$C_2B_{10}H_{12}$ isomerises to 1,12-$C_2B_{10}H_{12}$ only above 500°C. We have already noted that many thermal rearrangements involve electron transfer between occupied and unoccupied boundary molecular orbitals, which determines the course of the given reaction. In this case the excitation of the electron is apparently associated with an appreciable mutual approach of the HOMO and LUMO levels on deformation of the molecule as a result of the vibrational motion or collision of the molecules. In the limiting case in the transition state there is a possibility of degeneracy of the electronic state of the molecule. Since, according to the Jahn–Teller effect, the excitation of the electron is stereochemically equivalent to the addition of one or two electrons, the deformed molecule may be stabilised to a greater or lesser extent in the open state. The possibility of easy structural rearrangements of an excited molecule and the closure of the polyhedron in a direction which is not the same as that of its opening lead to the isomerisation of the initial molecule. The alternative model of the mechanism of thermal rearrangements is based on the familiar ideas concerning the occurrence of synchronous (concerted) reactions. In the absence of symmetry-dependent prohibitions the energy of the system varies smoothly along the reaction coordinate and does not require the mutual approach of the HOMO and LUMO energy levels.

Evidently, among all the possible deformations of the initial molecule leading to the final product, those which are consistent with molecular symmetry, are minimal, and have the lowest force constants will actually occur. Thus, when the mechanisms of thermal rearrangements are considered, it is useful to employ the second-order Jahn–Teller effect, which imposes certain symmetry-dependent limitations on "soft" deformations. In conformity with this effect, the deformation should not be fully symmetrical and its representation should be included in the product of the representations of boundary molecular orbitals (see Section III).

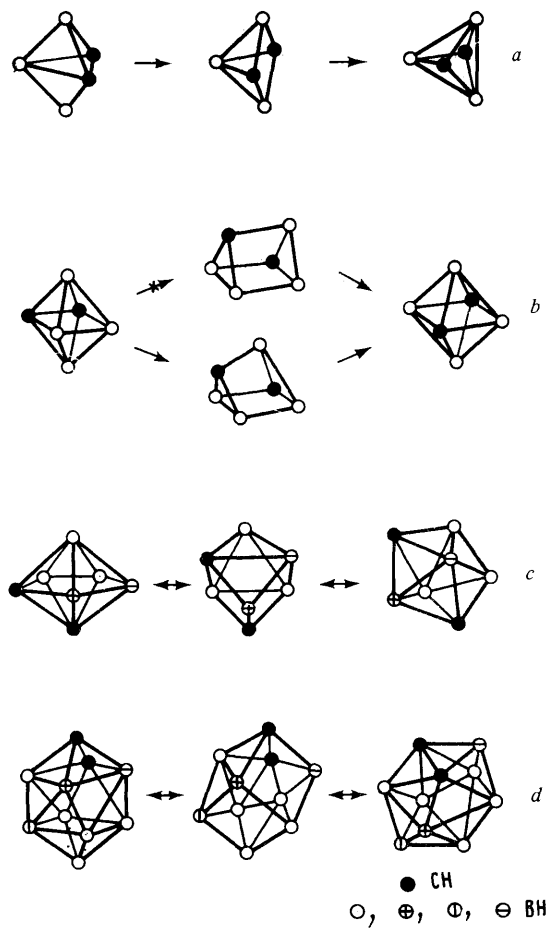


Figure 14. The proposed mechanisms for the thermal rearrangements of *closo*-carbaboranes with different structures: *a*) trigonal bipyramid; *b*) octahedron; *c*) pentagonal bipyramid; *d*) square antiprism with two vertices. In order to represent the rearrangements with greater clarity, the boron atoms in structures *c* and *d* are marked in different ways.

When the system attains equilibrium, the thermodynamically most stable isomer predominates. In the series of carbaboranes the tendency determining the direction of the rearrangement is the endeavour by carbon atoms to occupy positions in which their excess positive charge is compensated to the maximum extent and the molecule has the highest symmetry. This determines the high stability of isomers in which carbon atoms are furthest apart and have the minimum possible coordination number[2,136].

Trigonal bipyramid $C_2B_3H_5$. Dicarba-*closo*-pentaborane(5) has the structure of a trigonal bipyramid. In this structure there is a possibility of three isomers depending on the positions of the carbon atoms in the molecule. According to molecular orbital calculations, the thermodynamic stabilities of the isomers decrease in the sequence 1,5- > 1,2- > 2,3-$C_2B_3H_5$.[20] Only the two isomers 1,5- and 1,2-$C_2B_3H_5$ are known and the latter has been obtained only as the 2,3-dimethyl derivative, 2,3-Me_3-1,2-$C_2B_3H_5$, which does not rearrange to the 1,5-isomer and this served as the basis for the hypothesis that it is stabilised by the presence of methyl substituents[3,137]. The fact that 1,5-$C_2B_3H_5$ is formed in the reaction of diborane or pentaborane(9) with acetylene or in the pyrolysis of the *nido*-carbaborane 2,3-$C_2B_4H_8$, in which the carbon atoms occupy adjacent positions, indicates the intermediate formation of the $C_2B_3H_5$ isomers with carbon atoms in adjacent positions, i.e. 1,2- and (or) 2,3-$C_2B_3H_5$. Under reaction conditions, they rapidly isomerise to the thermodynamically more stable 1,5-isomer[137].

The mechanism of the rearrangements in the systems considered has not been investigated. A possible mechanism involves the rearrangement of the rhomboid fragment, made up of two trigonal faces, to a square, this being followed by the closure of the structure and the reformation of a rhomboid fragment in which the carbon atoms are separated by boron atoms—a *dsd* mechanism (Fig. 14*a*).[3]

Octahedron. $C_2B_4H_6$. An example of a rearrangement of an octahedral molecule is provided by the isomerisation of 1,2-$C_2B_4H_6$ to the 1,6-isomer, which occurs at 250°C.[138] Calculations show that the 1,6-isomer is more stable than the 1,2-isomer by 15 kcal mole^{-1},[139] which agrees with the direction of isomerisation. Lipscomb and coworkers[36] established by molecular orbital calculations that the rearrangement proceeds via the intermediate formation of a compound having the structure of a distorted trigonal prism (Fig. 14*b*). Mechanisms based on the formation in the transition state of a molecule with the structure of a non-distorted trigonal prism or on the opening of the *closo*-molecule to give a *nido*-structure, i.e. a pentagonal pyramid, are ruled out, since they require high activation energies[35,36].

Pentagonal bipyramid. $C_2B_5H_7$. Of the four possible $C_2B_5H_7$ isomers, two have been obtained so far: 2,3-$C_2B_5H_7$[62,122] and 2,4-$C_2B_5H_7$.[125] Rearrangements of this type of polyhedron have not been observed in the series of unsubstituted carbaboranes, although the 2,4-isomer should apparently be more stable. Lipscomb[3] proposed a two-stage mechanism for the possible rearrangement of the 2,3-isomer to 2,4-$C_2B_5H_7$, involving successive application of the *dsd* model (Fig. 14*c*) (see also subsection 3 of this Section).

Dodecahedron. $B_8H_8^{2-}$, $C_3B_5H_7$, and $C_2B_6H_8$. It has been noted that polyhedral systems of this type can readily undergo structural rearrangements of the atoms of the skeleton[140]. The influence of solvents, counterions, and temperature on the nature of the dynamic processes in the system has been investigated by ^{11}B NMR for the anion

$B_8H_8^{2-}$.[141] In solvents of low polarity at a temperature below 10°C the ^{11}B NMR spectrum has three signals with relative intensities of 2 : 4 : 2. On passing to highly polar solvents or on raising the temperature, the spectrum is gradually transformed and at 46°C in 1,2-dimethoxyethane it contains only signal. According to the authors [141,142], these data show that $B_8H_8^{2-}$ in solution has the structure of a trigonal prism with two vertices (solvents of low polarity, low temperature) or a square antiprism (polar solvents, elevated temperature) and not a dodecahedron (Fig. 15*a*). We believe that this interpretation of spectroscopic data is insufficiently justified. For example, the authors' assumption[141] that a change of temperature can lead to a complete conversion of one polyhedral form into another under the conditions of equilibrium between the suggested structures of a trigonal prism with two vertices and a square antiprism is incomprehensible. There is no doubt that rapid rearrangements of the polyhedral molecule (dynamic processes) are characteristic of the given system.

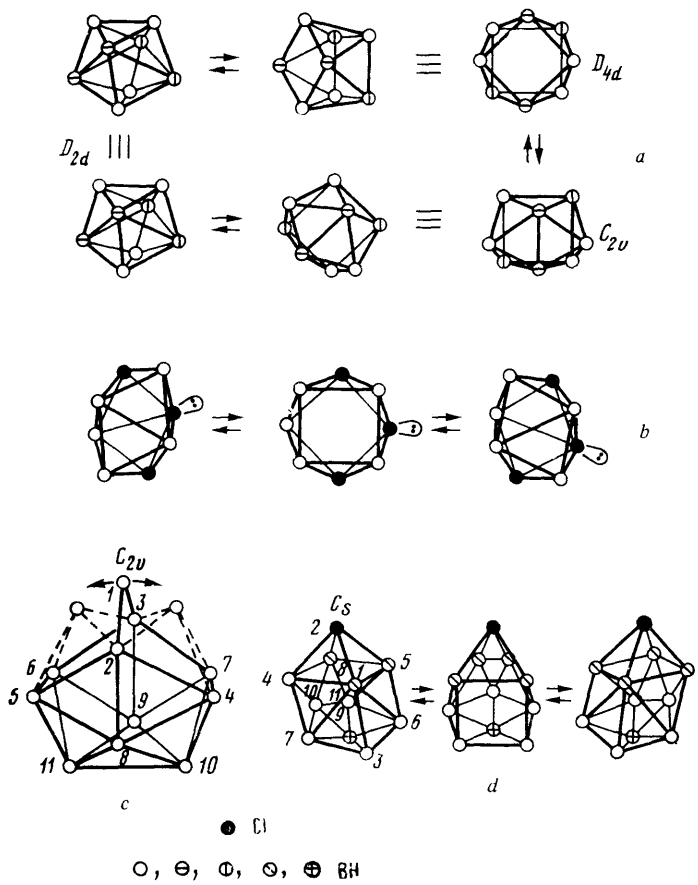


Figure 15. The proposed mechanisms for the dynamic rearrangements of certain closed polyhedral compounds: a) $B_8H_8^{2-}$; b) $C_3B_5H_7$; c) $B_{11}H_{11}^{2-}$; d) $CB_{10}H_{11}^{-}$. To achieve a greater clarity in the representation of the rearrangements, the boron atoms in structures *a* and *d* are marked in different ways.

$C_3B_5H_7$. Tricarba-*closo*-octaborane(7) is a second example of the occurrence of rapid rearrangements of the skeleton of an eight-atom polyhedral molecule. The ^{11}B NMR spectrum of this compound contains three signals with relative intensities 2 : 2 : 1, while the ^1H NMR spectrum consists of three quartets, due to protons linked to the boron atoms, and [a single] signal originating from the proton in the C–H bond with relative [H–B/H–C] intensities of 5 : 2. In order to account for the spectroscopic data, the authors[143] postulate the occurrence of dynamic rearrangements of the molecule with a dodecahedral structure via a transition state having the structure of a square antiprism (Fig. 15*b*).

One may assume that such easy rearrangements in the compounds considered are caused either by the degeneracy of the ground molecular state or by the low value of the energy gap between HOMO and LUMO and, in conformity with the Jahn–Teller effects, the configurational instability of the molecules.

$C_2B_6H_8$. Only one isomer (1,7-$C_2B_6H_8$) of dicarba-*closo*-octaborane(8) has been obtained. According to X-ray diffraction data, it has the structure of a dodecahedron (D_{2d} symmetry). Although the ^{11}B NMR spectrum of 1,7-$C_2B_6H_8$ has only two signals with relative intensities of 4 : 2, the authors[58,142] suggest that this compound undergoes dynamic rearrangements of its molecular skeleton and that the presence of the signal with a relative intensity of 4 is due to a random superposition of two signals having relative intensities of 2 : 2.

Square antiprism with two vertices. $C_2B_8H_{10}$. Of the seven possible isomers of dicarba-*closo*-decaborane(10), only three are known at the present time: 1,2-, 1,6- and 1,10-$C_2B_8H_{10}$. As was to be expected, the stabilities of these isomers increase in the sequence 1,2- < 1,6- < 1,10-$C_2B_8H_{10}$. The compounds 1,2- and 1,6-$C_2B_8H_{10}$ wholly isomerise to the 1,10-isomer on heating to 300°C.[58,88] The mechanism proposed for the rearrangements is based on the *dsd* model and requires several consecutive stages (Fig. 14*d*).[3]

Octadecahedron. $B_{11}H_{11}^{2-}$, $CB_{10}H_{11}^{-}$, and $C_2B_9H_{11}$. As for the dodecahedron, the rearrangement of polyhedral compounds having the structure of an octahedron proceed very readily.

$B_{11}H_{11}^{2-}$. The ^{11}B NMR spectrum of *closo*-undecaborate(2-) contains only one signal[144] and its nature is independent of the solvent employed and the temperature[145]. A decrease of temperature causes only a broadening of the signal in the spectrum, apparently due to the increased viscosity of the solution. Analogous data were obtained for $B_{11}H_7Br_4^{2-}$. The ^{11}B NMR spectrum of this compound has two signals with relative intensities of 4 : 7, caused by substituted and unsubstituted boron atoms. Tolpin and Lipscomb[145] explained the results on the hypothesis that these ion rapidly rearrange in solution via a transition state with the structure of an 11-vertex fragment of an icosahedron (Fig. 15*c*).

$CH_{10}H_{11}^{-}$. Another mechanism of the rearrangement of molecules having an octadecahedral structure has been proposed[146] in a study of monocarba-*closo*-undecaborate(1-). This mechanism is based on the *dsd* model. The ^{11}B NMR spectrum of this compound is characterised by three signals with relative intensities of 1 : 5 : 4, which can be explained by a rapid rearrangement (Fig. 15*d*). As

a result, the boron atoms in the 1-, 4-, 5-, and 8-positions and those in the 3-, 6-, 7-,10-, and 11-positions are indistinguishable in their spectral effects, while the $B_{(9)}$ atom gives rise to a single-intensity signal[146]. It is noteworthy that both mechanisms considered yield equally satisfactory explanations of the observed ^{11}B NMR spectra of $B_{11}H_{11}^{2-}$ and $CB_{10}H_{11}^{-}$.

As in $B_8H_8^{2-}$, the dynamic processes in $CB_{10}H_{11}^{-}$ and $B_{11}H_{11}^{2-}$ are apparently caused by the degeneracy of the ground state or the proximity of the boundary orbitals of the molecule. The lack of data for the energies and symmetries of the molecular orbitals of these compounds makes it impossible at the present time to give preference to one of the two mechanisms proposed for the rearrangements. However, if the deformation leading to the opening of $B_{11}H_{11}^{2-}$ (C_{2v}) and $CB_{10}H_{11}^{-}$ (C_S) has B_2 and A'' symmetry respectively, then the deformation characterising the *dsd* model does not correspond to any of the normal vibrations of the molecules under consideration. On the assumption that the excitation energy required for the rearrangement of the molecule is distributed among the normal vibrational degrees of freedom and that the deformation in the direction of the soft vibrational mode leads to rearrangement, this nevertheless enables us to consider the "opening-closure" mechanism to be more probable for the rearrangements of $B_{11}H_{11}^{2-}$ and $CB_{10}H_{11}^{-}$.[63]

2,3-$C_2B_9H_{11}$. 2,3-Dicarba-*closo*-undecaborane(11) is the only one of the twenty possible isomers obtained at the present time and is theoretically the most stable. This carbaborane is formed from both 7,9-$C_2B_9H_{13}$ and 7,8-$C_2B_9H_{13}$ in which the carbon atoms are in adjacent positions[58]. In the latter case the carbon atoms in the $C_2B_9H_{11}$ formed in the first stage should also apparently be in adjacent positions and the structure is possibly 2,4-$C_2B_9H_{11}$. Its rapid isomerisation to the 2,3-isomer is consistent with the ease of the rearrangements of octadecahedral molecules.

Icosahedron. $C_2B_{10}H_{12}$ and $CHPB_{10}H_{10}$. Numerous studies have been devoted to the thermal rearrangements of carbaboranes(12) and their derivatives. It has been established that the thermodynamic stability of $C_2B_{10}H_{12}$ isomers increases in the sequence 1,2- < 1,7- < 1,12-$C_2B_{10}H_{12}$, and that at approximately 450° C the *o*-isomer isomerises wholly to the *m*-isomer.[147-151] The *p*-isomer is formed at a higher temperature (approximately 600° C and above)[152] and equilibrium is established between the *m*- and *p*-carbaboranes(12)[153]:

$$1,2\text{-}C_2B_{10}H_{12} \xrightarrow{450^\circ} 1,7\text{-}C_2B_{10}H_{12},$$

$$1,7\text{-}C_2B_{10}H_{12} \underset{}{\overset{600^\circ}{\rightleftharpoons}} 1,12\text{-}C_2B_{10}H_{12}.$$

The introduction of bulky substituents into the icosahedral molecule led to a considerable facilitation of the rearrangements in many instances[154].

As a result of systematic studies on the rearrangement of carbaborane(12) isomers their B-halogeno-derivatives, and other icosahedral heteroboranes, six different mechanisms have been suggested to account for the formation of the products of the rearrangement (Fig. 16). The mechanism involving a cubo-octahedral transition state (Fig. 16*a*) explains the formation of 1,7-$C_2B_{10}H_{12}$ from the 1;2-isomer, but cannot account for the formation of 1,12-$C_2B_{10}H_{12}$.[3,34,155,156] The mechanism which is also based on a cubo-octahedral transition state but is modified by the assumption that the trigonal faces in the latter can rotate (Fig. 16*b*) explains the formation of 1,12-$C_2B_{10}H_{12}$ and the composition of the isomer mixture formed in the rearrangements of 9-Br-1,2-$C_2B_{10}H_{11}$[157] and 9-Cl-1,7-$C_2B_{10}H_{11}$.[158] In another modification of the *dsd* mechanism the rotation of tetragonal faces in the transition state is postulated (Fig. 16*c*).

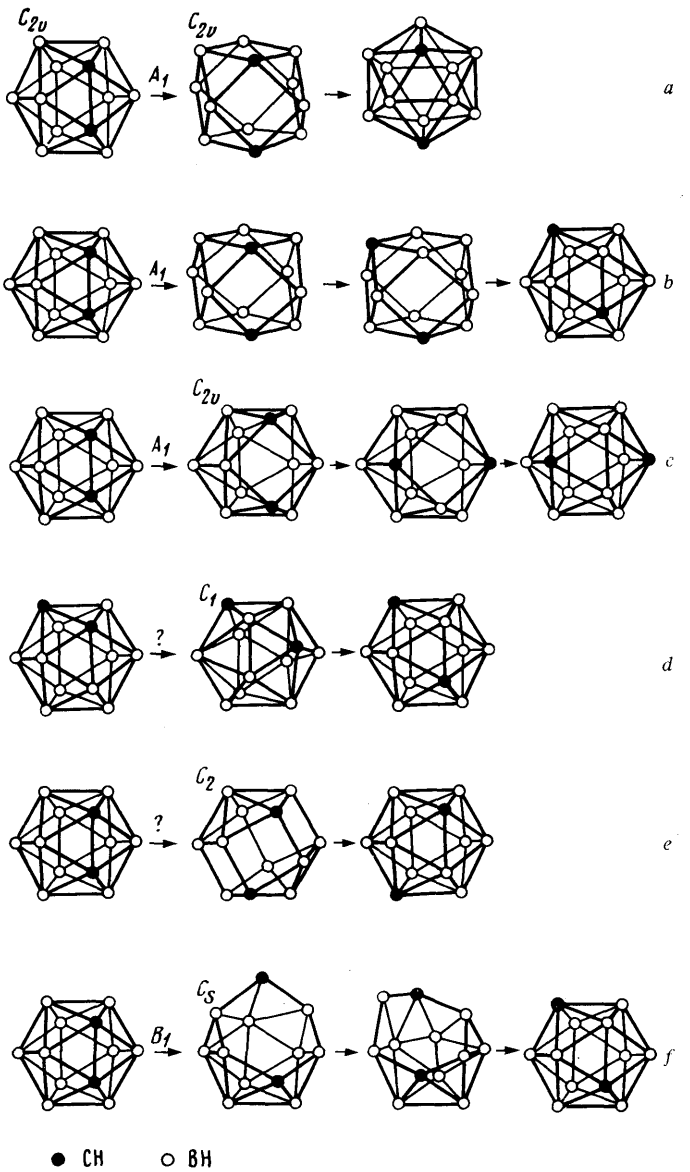


Figure 16. The mechanisms proposed for the rearrangements of icosahedral carbaboranes.

This mechanism has been proposed as one capable of explaining the rearrangements in the series of phosphacarbaboranes[5]. The last two mechanisms involve the rotation of trigonal faces (Fig. 16*d*) and pentagonal pyramidal fragments (Fig. 16*e*) in the ground icosahedral state[6,7]. These mechanisms also explain the formation of 1,12-$C_2B_{10}H_{12}$ and preference is given to the mechanism based on the rotation of pentagonal pyramids in the rearrangement of *B*-halogenophosphacarbaboranes[5]. Thus, according to the

authors[5], the mechanism of the rearrangements of icosahedral molecules should change on passing from the carbaborane system $C_2B_{10}H_{12}$ to the heterocarbaborane system $CHPB_{10}H_{10}$.

Wong and Lipscomb[5] proposed a mechanism for the rearrangements of icosahedral molecules which differs fundamentally from that considered above. It involves the opening of the icosahedral *closo*-structure to give a *nido*-structure which is a fragment of a 13-vertex polyhedron; the reverse closure of the polyhedron in other directions leads to the formation of different isomeric products (Fig. 16*f*). Since this mechanism predicted the occurrence of certain isomers whose formation in the series of phosphacarbaboranes had not been observed experimentally, the authors[5] gave preference to the mechanism involving the rotation of pentagonal pyramidal fragments. However, it is evident that, without the imposition of boundary conditions, the "opening-closure" mechanism, being one of the most general, will predict the formation of all possible isomers.

It was already noted above that the mechanisms involving a cubo-octahedral transition state do not meet the requirements of the symmetry of "soft" deformations. Indeed, if the molecules of 1,2- and 1,7-$C_2B_{10}H_{12}$ with C_{2v} symmetry are considered, the deformation leading to a cubo-octahedral transition state has the A_1 symmetry, i.e. is fully symmetrical (Figs. 16*a*, 16*b*, and 16*c*). On the basis of the symmetry I_h of a regular icosahedron ($B_{12}H_{12}^{2-}$), one can also conclude that this mechanism as well as the mechanism based on the rotation of pentagonal fragments are unlikely, since the direct product of the representations of the boundary orbitals of $B_{12}H_{12}^{2-}$ having the G_u symmetry for HOMO and G_g symmetry for LUMO[14,18] is equal to $A_u + F_{1u} + F_{2u} + G_u + H_u$, i.e. includes only representations which are antisymmetric relative to the inversion operation. On the other hand, the deformations considered are symmetrical relative to inversion (Figs. 16*a* and 16*e*) and their representations cannot therefore be included in the above product. The mechanisms involving the rotation of individual fragments of the icosahedral molecule (Figs. 16*d* and 16*e*) are also unlikely, since in the molecules with the given symmetry there are no normal vibrations corresponding to the required deformations. Furthermore, the mechanisms considered above require large displacements of many atoms. On the other hand, the deformation leading to the opening of the molecule (Fig. 16*f*) has the B_1 symmetry, if one begins with the C_{2v} symmetry for 1,2- and 1,7-$C_2B_{10}H_{12}$, and is minimal.

2. REARRANGEMENTS OF OPEN POLYHEDRAL MOLECULES

As already mentioned, the structures of *nido*-compounds are n-vertex fragments of an $(n + 1)$-vertex closed polyhedron and are characterised by the presence of a tetragonal, pentagonal, or hexagonal face. Neutral polyhedral *nido*-compounds are also characterised by the presence of hydrogen bridge atoms§ in the open face, which determines their thermal instability—*nido*-carbaboranes decompose on heating with evolution of hydrogen and give rise to *closo*-carbaboranes (see Section IV, subsection II).

Thermal rearrangements of *nido*-carbaboranes have been observed only for the corresponding anions. Among the possible conformers, those with the maximum possible number of atoms in the open face are stable on thermal isomerisation. The relative thermodynamic stabilities of isomers with different positions of the heteroatoms in the molecule are determined, as already mentioned, by the possibility of compensating their excess charge. Accordingly, in the thermodynamically more stable *nido*-carbaboranes the carbon atoms are as a rule located in the open face.

Tetragonal pyramid. $C_2B_3H_7$. A distinctive feature of the familiar 1,2-$C_2B_3H_7$ isomer of dicarba-*nido*-pentaborane(7) is that only one carbon atom is located in the open face of the molecule and the second occupies a vertex position (Fig. 17*a*).[159] The stability of this particular isomer can be accounted for by the presence of two hydrogen bridge atoms. If both carbon atoms were in the open tetragonal face, then, in view of the necessity for the formation under these conditions of a CHB bridge, the excess positive charge on the carbon atom would have increased and not decreased. On the other hand, the formation of the BH_2 or CH_2 group is unfavourable in view of the principle governing the stability of polyhedral compounds¶. For this reason, only the 1,2-isomer of the neutral *nido*-carbaborane $C_2B_3H_7$ exists[10]. According to molecular orbital calculation, the dianion $C_2B_3H_5^{2-}$ should also have the structure of a tetragonal pyramid and the stability of the isomers should then vary in the sequence 2,4- > 2,3- > 1,2-$C_2B_3H_5^{2-}$ according to general principles. Calculation shows that the rearrangement of one isomer to another takes place as a result of the migration of an atom from the open face to the site of the missing vertex of the octahedron. This mechanism is symmetry-allowed and energetically more favourable than the *sds* (*square–diamond–square*) mechanism, which is also symmetry-allowed[10].

Pentagonal pyramid. $C_2B_4H_8$. Although two of the three possible isomers of dicarba-*nido*-hexaborane(8), with neighbouring or non-neighbouring carbon atoms in the open pentagonal face, are known (the 2,3- and 2,4-isomers†) (Fig. 17*b*), there are no literature data for the rearrangement of one isomer to the other. At the same time rearrangements of substituted carbaboranes with retention of the positions of the carbon atoms have been observed[65,110,111]:

$$5\text{-}Me_3N\text{-}2,4\text{-}C_2B_4H_6 \rightarrow 3\text{-}Me_3N\text{-}2,4\text{-}C_2B_4H_6\ ,$$
$$4\text{-}R_3Si\text{-}2,3\text{-}C_2B_4H_7 \rightarrow 1\text{-}R_3Si\text{-}2,3\text{-}C_2B_4H_7\ .$$

Calculation showed that the stabilities of the isomeric dianions vary in the sequence 2,4- > 2,3- > 1,2-$C_2B_4H_6^{2-}$.[10]

$C_2B_6H_{10}$. The proposed structure of the known isomer of dicarba-*nido*-octaborane(10) (I) is presented in Fig. 17*c*. ^{11}B and ^1H NMR data are also consistent with the possibility of dynamic transitions between structures (II) and (II′) (Fig. 17*c*).[160]

§ In conformity with the isoelectronic principle, certain *nido*-compounds, for example, *nido*-carbaboranes $C_4B_{n-4}H_n$, are uncharged and have no hydrogen bridge atoms.

¶ Polyhedral systems where, as far as possible, all the $3n$ orbitals of the atoms in the skeleton are involved in the formation of bonds are distinguished by the highest stability.

† The 2,4-isomer is known only as the anion 2,4-$C_2B_4H_7^-$ or the inner trimethylammonium salt[109,110].

$C_2B_7H_{11}$. Dicarba-*nido*-nonaborane(11) is interesting because its structure is greatly influenced by substituents at the carbon atoms of the molecular skeleton. Thus the possible structure of the unsubstituted carbaborane $C_2B_7H_{11}$ (the known isomer) (Fig. 17*d*) is characterised, according to the authors[62], by the presence in the open hexagonal face of two carbon atoms in the *ortho*-positions with respect to one another, and of only one BHB bridge. According to ^{11}B NMR data, another "superfluous" hydrogen atom forms a σ bond with a boron atom, giving rise thereby to the BH_2 structural unit. When methyl substituents are attached to the carbon atoms, the molecule has the usual structure of a fragment of a square antiprism with two vertices according to X-ray diffraction data (Fig. 17*d*). The authors[62] explain the structural differences and the greatest stability of the dimethyl derivative of $C_2B_7H_{11}$ by the steric or electronic influence of methyl groups.

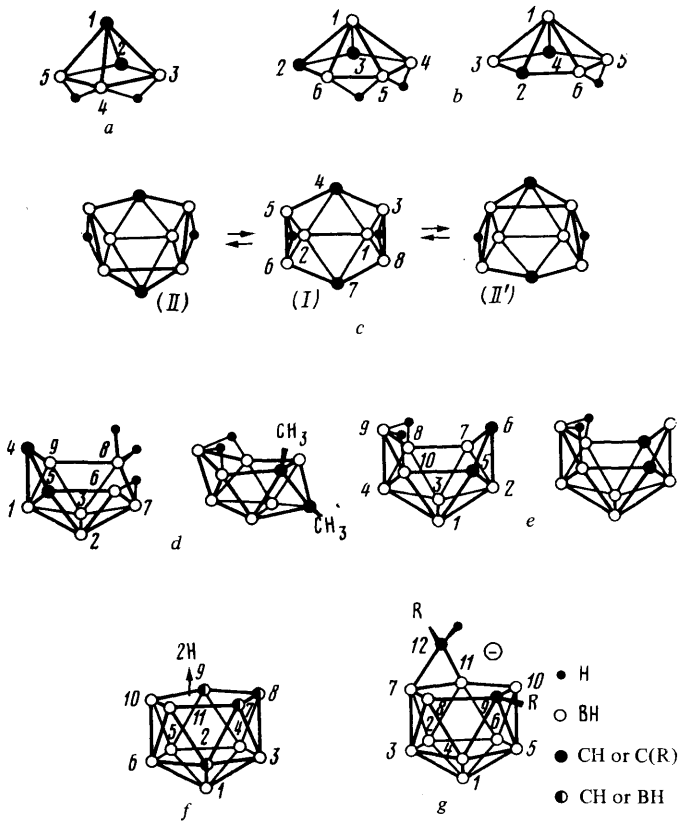


Figure 17. The structures of *nido*-carbaboranes: *a*) 1,2-$C_2B_3H_7$; *b*) 2,3-$C_2B_4H_8$ and 2,4-$C_2B_4H_7^-$; *c*) 4,7-$C_2B_6H_{10}$; *d*) 4,5-$C_2B_7H_{11}$ and 6,7-$Me_2C_2B_7H_9$; *e*) 5,6- and 5,7-$C_2B_8H_{12}$; *f*) 7,8-, 7,9-, 2,7-, 2,8- and 2,9-$C_2B_9H_{13}$; *g*) 9,12-$R_2C_2B_{10}H_{11}^-$ (R = Me or Ph).

$C_2B_8H_{12}$. Two isomers of dicarba-*nido*-decaborane(12) are known—with the carbon atoms in the open face occupying neighbouring positions (5,6-$C_2B_8H_{12}$)[62,122] and separated by one boron atom (5,7-$C_2B_8H_{12}$)[123] (Fig. 17*e*). Thermal rearrangements of $C_2B_8H_{12}$ isomers or their derivatives have not been noted.

$C_2B_9H_{13}$. Five isomers of dicarba-*nido*-undecaborane(13) are known at the present time: 7,8-, 7,9-‡, 2,9-, 2,8-, and 2,7-$C_2B_9H_{13}$ (Fig. 17*f*). These *nido*-carbaboranes are formed on protonation of the corresponding dicarba-*nido*-undecaborates(1-). The first three isomers are obtained on alkaline cleavage of 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$[161-163] and the last two are obtained as a result of chemically initiated thermal rearrangements occurring in the alkylation of 7,8- and 7,9-dicarbollide ions by alkyl halides[12,63,64,69].

Carrett and Hawthorne[164] achieved the thermal isomerisation of 7,8-$C_2B_9H_{12}^-$ to the 7,9-isomer:

$$7,8\text{-}C_2B_9H_{12}^- \xrightarrow{300^\circ} 7,9\text{-}C_2B_9H_{12}^-.$$

The rearrangements of dicarba-*nido*-undecaborates occur much more readily when their electronic structure is altered during the chemical reaction. Thus the rearrangement of the 7,8-isomer to the 2,7-isomer in the alkylation of 7,8-$C_2B_9H_{11}^{2-}$ is so fast that the intermediate Alk-7,8-$C_2B_9H_{11}^-$ cannot be detected even below 0°C:[12,69]

$$7,8\text{-}C_2B_9H_{11}^{2-} \xrightarrow{RX} (\text{R-7,8-}C_2B_9H_{11}^-) \rightarrow \text{11-R-2,7-}C_2B_9H_{11}^- .$$

The structure of 11-R-2,7-$C_2B_9H_{11}^-$ has been demonstrated, together with other methods, by a complete X-ray diffraction investigation of the corresponding protonated derivative 11-Me-2,7-$C_2B_9H_{12}$.[165] The intermediate product μ-Alk-7,9-$C_2B_9H_{11}^-$ of the alkylation of 7,9-$C_2B_9H_{11}^{2-}$ is relatively more stable and has been detected, but not isolated because it rearranges rapidly above 0°C:[64]

$$\begin{array}{l} \text{7-R-2,8-}C_2B_9H_{12} \\ {\scriptstyle +H+}\uparrow\downarrow{\scriptstyle -H+} \\ 7,9\text{-}C_2B_9H_{11}^{2-} \xrightarrow{RX} \mu\text{-R-7,9-}C_2B_9H_{11}^- \rightleftarrows (\text{7-R-2,8-}C_2B_9H_{11}^-) \xrightarrow{-H+} (\text{7-R-2,8-}C_2B_9H_{10}^{2-}) \rightarrow \\ \rightarrow \text{10-R-7,9-}C_2B_9H_{10}^{2-} \xrightarrow{+H+} \text{10-R-7,9-}C_2B_9H_{11}^- . \end{array}$$

In the 2,7- and 2,8-isomers of *B*-alkyldicarba-*nido*-undecaborate(1-) only one carbon atom is located in the open face; the other is in the closed part of the polyhedron, and this is the reason for the low stability of these isomers. The direction and rate of the rearrangements of the 2,7- and 2,8-$C_2B_9H_{13}$ derivatives are determined by the tendency to remove both carbon atoms to the open face and the substituent by the equatorial position when the process is stereospecific[63]. Thus 11-Me-2,7-$C_2B_9H_{12}$ is relatively resistant to rearrangements; the monoanion 11-Me-2,7-$C_2B_9H_{11}^-$ rearranges in solution at room temperature to 8-Me-7,9-$C_2B_9H_{11}^-$, while the dicarbollide ion 11-Me-2,7-$C_2B_9H_{10}^{2-}$ is converted in solution below −30°C (liquid ammonia) into 9-Me-7,8-$C_2B_9H_{10}^{2-}$, yielding 9-Me-7,8-$C_2B_9H_{11}^-$ after protonation (Fig. 18).[12,69] Among the 2,8-isomers, only the compound 7-Alk-2,8-$C_2B_9H_{12}$ is relatively resistant to rearrangements. When a proton is abstracted, the above equilibrium between μ-Alk-7,9- and 7-Alk-2,8-$C_2B_9H_{11}^-$ is displaced towards μ-Alk-7,9-$C_2B_9H_{11}^-$, but the rearrangement as a whole proceeds towards 10-Alk-7,9-$C_2B_9H_{11}^-$. We suggest that the final product is formed as a result of the abstraction of a proton from 7-Alk-2,8-$C_2B_9H_{11}^-$ by a solvent molecule or by a second reactant molecule; as in the isomerisation of 11-Alk-2,7-$C_2B_9H_{11}^-$ to 9-Alk-7,8-$C_2B_9H_{11}^-$ (Fig. 18), the dianion

‡The *nido*-carbaborane 7,9-$C_2B_9H_{13}$ is unstable, because two BHB bonds cannot be formed in the open face, and it has been characterised only in the form of a salt of the corresponding monoanion 7,9-$C_2B_9H_{12}^-$.[161]

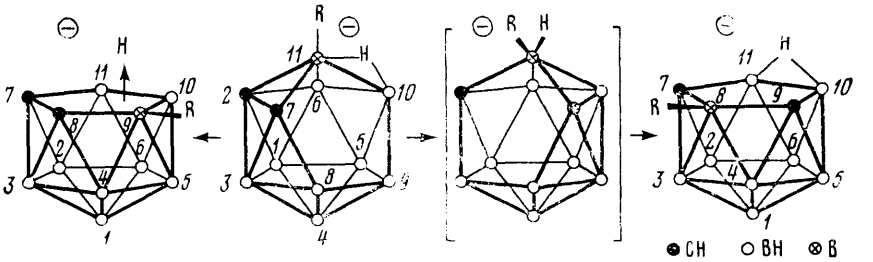


Figure 18. The possible modes of rearrangement of 11-R-2,7-$C_2B_9H_{11}^-$ (R = alkyl).

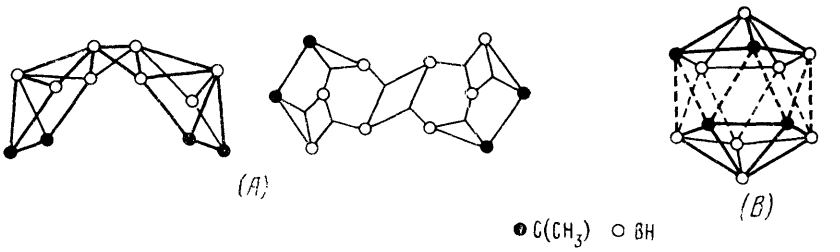


Figure 19. Structures proposed for the isomers of the four-carbon carbaborane $Me_4C_4B_8H_8$.

7-Alk-2,8-$C_2B_9H_{10}^{2-}$ rearranges to 10-Alk-7,9-$C_2B_9H_{10}^{2-}$. On protonation, the latter gives rise to 10-Alk-7,9-$C_2B_9H_{11}^-$.[63]

The rearrangements of 7,8- and 7,9-isomers to 2,7- and 2,8-dicarba-*nido*-undecaborates(1-), discussed above, are facilitated in reactions with electrophiles by the breakdown of the delocalisation of the electrons in the open face of dicarbollide ions and the axial orientation of the substituent on formation of a "π-complexes" and then a "σ-complex".[12] It is possible to distinguish two stages in these reactions: the first involving the addition of the electrophile to the dicarbollide ion (activation of the system) and the second involving a thermal rearrangement of the resulting dicarba-*nido*-undecaborate with an axially oriented alkyl group. Chemical activation is apparently energetically comparable to thermal activation and the rearrangements considered therefore proceed on the whole at lower temperatures.

$C_2B_{10}H_{14}$ derivatives. Owing to their low stability, neutral isomers of the *nido*-carbaborane $C_2B_{10}H_{14}$ have not been obtained. The anions of this carbaborane are relatively stable: the dianions, formed after the addition of two electrons to isomers of *closo*-$C_2B_{10}H_{12}$, and the monoanions obtained on protonation of the dianions. It was noted above that the dianions $C_2B_{10}H_{12}^{2-}$ are apparently not individual species, consisting of sets of dynamic structures based on the open structure of a fragment of a 13-vertex polyhedron. The rearrangements of the dianions are determined, on the one hand, by dynamic processes involving a change in the position of the vertex raised over the plane of the open face, as, for example, in the cobalt complex of the carbaborane ligand $C_2B_{10}H_{12}^{2-}$ (Fig. 20*e*)[166] and, on the other hand, they are determined by the migration of one of the atoms in the open face to the site of the missing vertex of the polyhedron. This type of rearrangement explains the transitions between different sets of dynamic structures, for example, in the isomerisation of the dianions obtained from *o*-, *m*-, and *p*-carbaboranes(12) and their derivatives (Fig. 10). A process with "closure-opening" of the polyhedral system is also possible.

Protonation of the dianions $C_2B_{10}H_{12}^{2-}$ and their derivatives leads to the fixation of the open face and the monoanions can be isolated as individual compounds. On heating to 100°C, one of the isomers isolated is converted quantitatively into the other[76,77]. Depending on the direction of electrophilic attack by the proton, the open structure of the dianion should be retained in its entirety, if the proton occupies a BHB bridge position, or closed to a greater or lesser extent on formation of a B–H or C–H σ bond[2]. The latter process takes place as a result of the transfer of an electron pair from the orbital binding the atoms of the molecular skeleton to an outer σ bond. This type of closure has been demonstrated by an X-ray diffraction study of one of the isomers C,C'-Me_2- and C,C'-Ph_2-$C_2B_{10}H_{11}^-$, which are characterised by the presence of the $C\begin{smallmatrix}R\\H\end{smallmatrix}$ structural unit (Fig. 17*g*).[167,168]

The closure of the structure of the dianion also occurs under the influence of other electrophiles. For example, the alkylation of the aminated dianions derived from 1,2-$C_2B_{10}H_{12}$ proceeds at the boron atom, and, when the latter migrates together with the substituent in the transition state, a hydride ion is evidently ejected (oxidised) from the boron atom with the alkyl group; the molecule undergoes closure to *closo*-2-NH_2-6-Alk-1,7-$C_2B_{10}H_{10}$.[169-172] This mode of reaction is apparently due to the increased hydride mobility of the hydrogen atom linked to the migrating boron atom attached to the substituent.

$Me_4C_4B_8H_8$. The synthesis of the stable four-carbon carbaborane $Me_4C_4B_8H_8$, isoelectronic with the $C_2B_{10}H_{12}^{2-}$ dianions, is of considerable interest in both theory and

practice[173-175]. In solutions $Me_4C_4B_8H_8$ exists in two equilibrium isomeric forms A and B:

$$A \rightleftarrows B,\ K = [B]/[A] = 0.5.$$

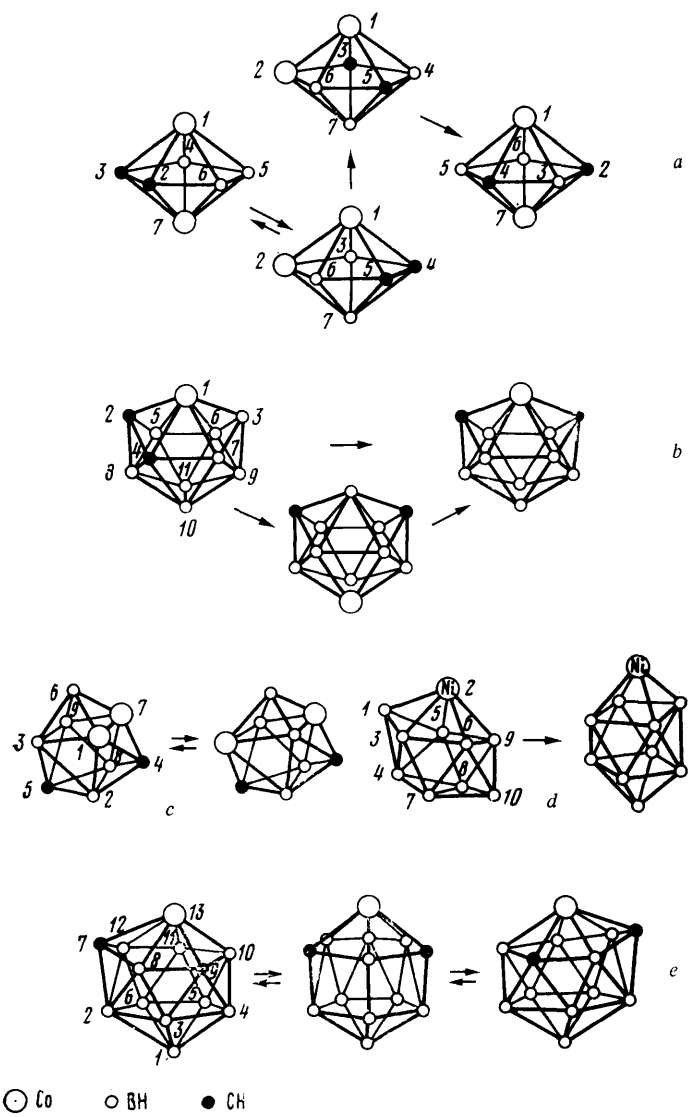


Figure 20. Thermal rearrangements of certain metallocarbaboranes: *a*) $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$; *b*) $(\eta^5\text{-}C_5H_5)CoC_2B_8H_{10}$; *c*) $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$; *d*) $(\eta^5\text{-}C_5H_5)NiB_9H_9^-$; *e*) $(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$. The ligands C_5H_5 are not shown in the Figure.

When the solvent is removed, the equilibrium is wholly displaced towards isomer A. The ^{11}B NMR spectrum of isomer A is characterised by four signals of equal intensity distributed over a wide frequency range. The ^1H NMR spectrum has two signals due to the protons of the methyl groups and these are also of equal intensity. The proposed geometrical and valence structure of isomer A is presented in Fig. 19.[174] Compound B is characterised by a more compact ^{11}B NMR spectrum, in which there are two signals with relative intensities of 6 : 2. The ^1H NMR spectrum of this isomer contains, like that of isomer A, two signals, which merge at 40°C into a single narrow signal. On the basis of these data, the authors[173-175] proposed for isomer B the structure of a somewhat distorted icosahedron, having assumed the possibility of the rotation of the pentagonal pyramidal fragments in order to account for the spectroscopic data (Fig. 19). Above we already discussed this mechanism of the rearrangement of icosahedral molecules in terms of the correspondence between the symmetry of "soft" deformations and the symmetry of molecular orbitals and concluded that it is unlikely (Section V, subsection 1). The Wade rule suggests that a *nido*-structure of the fragment of a 13-vertex polyhedron with four carbon atoms in the open face is more likely for the isomers of $Me_4C_4B_8H_8$. Here account must also be taken of the possibility of some deformation of the open face of the molecule, associated, for example, with its narrowing. As a result of such deformation, the excess charge on the carbon atoms might be compensated to a greater extent. The interconversions of the isomers of $Me_4C_4B_8H_8$ can proceed either via a transition state having a structure close to that of the icosahedron, or as a result of consecutive migrations of the atoms in the open face to the sites of the missing vertex of the polyhedron.

3. REARRANGEMENTS OF METALLOCARBABORANES AND METALLOBORANES

The thermal rearrangements of metallocarbaboranes and metalloboranes have many features which are not characteristic of, for example, carbaboranes and are therefore considered separately in this review.

In their studies of the rearrangements of metallocarbaboranes containing between six and ten boron atoms and between one and three cobalt atoms Hawthorne and coworkers[176-178] derived the following empirical rules defining the direction of the rearrangements:

(a) the cobalt atom migrates to the vertex with the maximum coordination number and subsequently remains in this position;

(b) the carbon atoms in the skeleton do not approach one another;

(c) carbon migrates irreversibly to the vertex with the minimum coordination number;

(d) a carbon atom tends to migrate away from a cobalt atom if rules (b) and (c) hold.

Grimes and coworkers[179-181] fully confirmed the validity of these rules for metallocarbaboranes containing between three and five boron atoms, noting at the same time a number of features. Thus, during the rearrangement of $1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ there is successive formation of $1,2,4,5\text{-}$ and $1,2,3,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, in which the cobalt atom occupies the position with the smallest coordination number (C.N.) and the rearrangement occurs only at a higher temperature, as a result of which the cobalt atom again occupies the position with the maximum coordination number (Fig. 20*a*).[179] The intermediate formation of the metallocarbaborane isomer in which cobalt has the smallest coordination number was also noted in the isomerisation of $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Co\text{-}2,4\text{-}Me_2C_2B_8H_8$ (Fig. 20*b*).[180] These examples show that many rearrangements of metallocarbaboranes proceed via a series of stages. The problem of the mechanism of the rearrangements has not been discussed in most studies owing to the insufficiency

of experimental data. A mechanism based on the *dsd* model is possible. For the rearrangement of 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (Fig. 20*a*), Miller and Grimes [179] give preference to the mechanism involving the rotation of the trigonal faces of the polyhedron, noting correctly that this process, instead of being synchronous, may be a result of several consecutive stages, for example two *dsd* stages or, what is more probable, may occur via an open polyhedral intermediate [179]. A tendency of cobalt atoms to form Co–Co bonds was also noted, but in many instances it is compensated by the effect involving the repulsion of the cyclopentadienyl ligands. This in fact explains attainment of equilibrium between the two isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$ (Fig. 20*c*). [179,181]

An interesting rearrangement has been observed for the nickel–borane complex $(\eta^5\text{-}C_5H_5)NiB_9H_9$. In solution after brief heating to 150°C or irradiation with ultraviolet light the complex, in which the nickel atom occupies the position with the highest coordination number, undergoes quantitative isomerisation to a complex with four-coordinated nickel (Fig. 20*d*). [182] Thus, together with the features noted above, there is apparently a tendency towards the formation of a more symmetrical structure as a result of the rearrangement, in which there is a possibility of a greater delocalisation of electrons.

An interesting example of the configurational instability of a metallocarbaborane molecule is the 13-vertex cobaltcarbaborane 13,7,9-$(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$; in its solution there are rapid dynamic rearrangements between two enantiomers (Fig. 20*e*), which is manifested by the averaging of the NMR spectra of this compound. With decrease of temperature, the rate of the transitions diminishes and at −90°C the ^{11}B NMR spectrum indicates the absence of symmetry elements. The mechanism of the rearrangement is based on the *dsd* model and involves successive or synchronous formation of two tetragonal faces in the transition state (Fig. 20*e*). [166] The position of the above equilibrium is significantly influenced by substituents. Thus the introduction of a methyl group at one of the carbon atoms shifts the equilibrium towards the isomer in which the unsubstituted carbon atom occupies the position with the smallest coordination number [176].

In general, when the mechanisms of the rearrangements of metallocarbaboranes and metalloboranes are discussed, it is important to take into account the symmetry of the molecule, as for other polyhedral systems.

VI. CONCLUSION

In our discussion of the rearrangements of polyhedral molecules, we endeavoured in the first place to represent the characteristic features of the chemical behaviour of the compounds as the characteristic properties of carbaboranes, boron hydrides, and heteroborates, i.e. we tried to consider them as manifestations of the characteristics of the electronic structures of polyhedral boron compounds. The theoretical models which we employed, such as the model involving electrophilic reactions via two-centre bonds and nucleophilic reactions via three-centre bonds, can be useful only if one clearly realises the limits of their applicability. The latter depend in their turn on the validity in each specific case of concepts such as those of localised two-, three-, and many-centre bonds. Their energetic characteristics are also important. We believe that in a qualitative treatment the models employed are fully justified.

The presence of symmetry elements in the molecules and ions of polyhedral boron compounds and hence the symmetry of the electronic Hamiltonian permit a significant simplification of the selection of the possible directions and mechanisms of many of their reactions and in the first place their thermal rearrangements. In many cases it is sufficient for this purpose to consider the symmetry of the initial molecule and the symmetry of the deformation characterising the given mechanism of the rearrangement. In the more general case it is necessary to know the symmetry of the molecular orbitals, their energies, populations, as well as the types of the normal displacements possible in the given molecule or ion.

In general the use of fundamental concepts, such as the occurrence of the reactions as a result of the interaction of the bonding and antibonding orbitals of the reactants and the decisive role of the energy and symmetry of the boundary orbitals of the reactants and the transition state in determining the direction of the reaction, appear to be most promising in a qualitative discussion of the chemical properties of polyhedral boron compounds.

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During the preparation of this review for the press, certain fundamentally important reports devoted to the structures and rearrangements of polyhedral boron compounds were published. Here mention should be made in the first place of the papers by Lipscomb and coworkers [183–185]. Continuing their fundamental studies, the authors carried out quantum-chemical calculations (by the PRDDO method) on the closed borane anions $B_nH_n^{2-}$ and carboboranes $C_{2n}B_nH_{n-2}$ and found that they have localised valence structures, which can be represented by fractional bonds [183]. A topological analysis has been carried out and preliminary calculations have been made for the structures of closed boron hydrides containing between 13 and 24 atoms in the polyhedron and the possible methods of synthesis of such polyhedral compounds have been classified [184]. In order to investigate the rearrangements of polyhedral boron compounds, calculations have been made on the configurational behaviour of the anion $B_{11}H_{11}^{2-}$. [185] Grimes and coworkers [186–189] continued their studies on the four-carbon carbaborane $Me_4C_4B_8H_8$ and transition metal complexes of polyhedral compounds. An X-ray diffraction study has been made of one of the isomers of $Me_4C_4B_8H_8$ [186] and a number of complexes based on it, and their structural rearrangements have been investigated [187,188]. X-Ray diffraction analysis also made it possible to demonstrate that one of the boron atoms in the complex $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, formally containing $2n$ electrons binding the atoms of the molecular skeleton, is located above the plane [189]. Mikhailov and coworkers achieved the rearrangement of icosahedral carbaboranes under the influence of γ-radiation [90]. Photoinitiated rearrangements of nickel dicarbollide complexes have also been observed [191].

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Phosphorus Rings, Clusters, Chains, and Layers

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Phosphorus compounds with P-P bonds (polyphosphides, phosphanes, and organophosphorus compounds) are considered as compounds formed by ions or radicals with a skeleton† consisting of phosphorus atoms linked covalently to one another; the structure of such skeletons depends little on the nature of the ions or radicals attached to them. The simplest structurai elements of such skeletons have been isolated and the rules governing their combination into clusters, chains, layers, and cross-linked structures have been established. A classification is proposed and formulae are presented for homologous matrices of phosphorus skeletons and the wide variety of their structures is demonstrated. Certain aspects of the stereochemistry of polyphosphorus compounds are discussed. Its general features and the way it differs from the stereochemistry of organic compounds have been established. The considerable scope of the chemistry of polyphosphorus compounds is noted. The bibliography includes 47 references.

CONTENTS

I.	Introduction	153
II.	"Island" structures	154
III.	Chain structures	156
IV.	Layer structures	158
V.	Cross-linked structures	158
VI.	Conclusion	159
VII.	Appendix (determination of the structures of P_2^1 phosphorus skeletons)	160

I. INTRODUCTION

More than twenty years ago J.R.Van Wazer wrote in a foreward to his notable monograph of phosphorus chemistry "...there is a real need for a separate discipline just as there was a need for separating the chemistry of carbon compounds from the rest of chemistry. Instead of being merely a ragbag collection, the compounds of carbon are readily arranged into homologous series, and a small number of ground rules have proved sufficient to describe the relationships and interactions between these homologous series and between members of a given series. This state of affairs also seems to apply to the compounds of phosphorus... Furthermore, a system of ground rules, in some cases quite different from those of organic chemistry, appears to be emerging." (Van Wazer[1], p. 7).

The aim of the present review is to attempt to confirm the above words by analysing the characteristic features of the structure of skeletons consisting of two or more covalently linked phosphorus atoms in compounds of different classes: polyphosphides, phosphanes, and organophosphorus compounds. Analysis of structural data shows that the structure of the phosphorus skeletons in compounds of this kind depends little on the nature of the atoms or radicals joined to the skeleton.

Almost all the information about polyphosphorus compounds has been obtained in the last 15 years and nowadays this field of phosphorus chemistry is developing vigorously: it is therefore useful to examine critically and to arrange schematically the available literature data.

It is of interest to note that, despite the hypothesis of Krebs et al.[2] that many polyphosphides ($ZnPbP_{14}$, $HgPbP_{14}$) have a chain structure, and the available information concerning the complex allotropy of elemental phosphorus and about the existence of solid phosphorus hydrides and lower phosphorus oxides whose structure cannot be represented without assuming that phosphorus atoms are linked to one another, Van Wazer questioned the possibility of the existence of compounds involving a large number of covalently linked phosphorus atoms (Van Wazer[1], pp. 17, 123) and his view was shared by other workers[3,4].

More than 200 polyphosphorus compounds with skeletons comprising a finite (between 2 and 12) or an infinite number of phosphorus atoms are now known. On the other hand, the structures of only half of these compounds have been established, owing to the considerable difficulties of isolating and identifying the individual phases because of the slow attainment of equilibrium in the synthetic reactions, the simultaneous formation of a large number of different polyphosphorus compounds having similar physicochemical properties, and the tendency of the compounds to form amorphous or vitreous phases. However, even these experimental data are sufficient to demonstrate the exceptionally wide variety of the structures of phosphorus skeletons.

In this situation it is timely and useful to develop a classification and to determine the fundamental structural characteristics of the phosphorus skeletons. The first attempt at a classification of the compounds in terms of the structure of the phosphorus skeletons rather than the type of crystal lattice is due to Schnering[5], who achieved successful determinations of structures. However, his classification embraces only some of the polyphosphorus compounds (polyphosphides) and follows the relation between their structure and the structural elements of the lattices of white, red, and black phosphorus. We proposed a wider classification[6,7]; the present review is devoted to a detailed description of this classification and

† The absence of a generally accepted nomenclature in the description of compounds with element–element bonds (organic, cluster, and polymeric compounds of boron, sulphur, phosphorus, etc.) makes it difficult to choose names for groups comprising the atoms of an element joined together by chemical bonds and incorporated in a given compound as a polycation, a polyanion, or a neutral group. We decided to adopt the term "skeleton" for such groups, assuming that it will be understood unambiguously by specialists working in various fields of chemistry.

an examination of the fundamental characteristics of the structure of skeletons in the polyphosphorus compounds of different classes. The classification is based on: (a) quantum-chemical ideas about the configuration of valence orbitals and the length of bonds formed by atomic phosphorus as the structural element of the phosphorus skeletons (Van Wazer, p. 3); (b) the analysis of ~100 structures of different polyphosphorus compounds, invoking data for the structures of phosphorus compounds with bivalent electronegative elements incorporating $\rangle P-E-P\langle$ groups (where E = O, S, Se, or Te) having the same structures as some of the phosphorus skeletons; (c) certain stereochemical ideas in organic chemistry[8]. We shall now formulate the fundamental characteristics defining the structure of phosphorus skeletons.

1. The P–P bond is formed predominantly by p electrons, so that the phosphorus atoms involved in the formation of such bonds are formally tervalent‡. The σ-linked phosphorus atoms are separated by a distance of 2.17–2.30 Å, approximately equal to twice the covalent radius of phosphorus. A decrease of this distance indicates a certain amount of multiple bond character. However, such shortening of the bond is not characteristic of phosphorus and in the present review skeletons with bonds of this kind are not considered at all§. The valance angles of tervalent phosphorus are usually intermediate between 90° and 109°29′, corresponding to the p^3 and sp^3 states; in the P_3 group the valence angle is 60° ("bent" bonds).

2. The skeleton of a polyphosphorus compound can incorporate phosphorus atoms linked by a single bond with one, two, or three adjoining phosphorus atoms. We shall henceforth refer to such atoms as singly-linked ($\rangle P-P\langle$), doubly-linked ($\rangle P-\underset{|}{P}-P\langle$), and triply-linked ($\rangle P-\underset{|}{\underset{P}{P}}-P\langle$).[5] If the numbers of these atoms are designated by l, m, and n respectively, then a skeleton consisting of x phosphorus atoms and having y free bonds is described by the formula $P_x^y = (P'_l P''_m P'''_n)^{(2l+m)}$.

3. The fundamental structural elements of the phosphorus skeletons are simple chains of finite or infinite length and rings incorporating 3–6 or more atoms. If the frequency of such structural elements in various phosphorus compounds is adopted as a measure of their stability, then the rings should be more stable than the chains with the same number of atoms and among rings those which are five- and six-membered should be the most stable[1,9,10,12,13].

4. Simple chains and rings can play the role of independent phosphorus skeletons in polyphosphorus compounds or can be condensed into more complex skeletons having finite or infinite dimensions.

5. Phosphorus skeletons with infinite dimensions can be constructed by the regular or irregular condensation of structural elements. In the first case the skeletons present in crystalline phosphorus compounds or in crystalline allotropic modifications of elemental phosphorus are formed. In the second case the products are the skeletons of vitreous or amorphous phosphorus-containing phases.

A structural classification of the phosphorus skeletons in various polyphosphorus compounds is presented in the Table. The structures of the phosphorus skeletons presented in the text are illustrated by graph schemes. To facilitate the comparison of various layer or cyclic structures, the distances between neighbouring phosphorus atoms in certain schemes, which are not linked to one another, are represented by the same lengths as those between covalently linked phosphorus atoms. The filled, open, and half-filled circles in the schemes illustrate respectively triply-, doubly-, singly-linked phosphorus atoms. In analysing the structures of phosphorus skeletons having infinite dimensions, we shall confine ourselves to regular structures. The structures are described in terms of arbitrarily selected basic groups, whose repetition by translation or 180° rotation makes it possible to construct the entire structure; the basic groups in the graph scheme are enclosed by dashed lines.

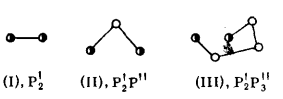
The characteristics of the structures of the phosphorus skeletons of each type are discussed below.

II. "ISLAND" STRUCTURES

We shall assign to "island" structures phosphorus skeletons having finite dimensions: simple chains, rings, clusters, and skeletons formed by the condensation of these simplest elements.

Simple Chains

The successive linking of phosphorus atoms can lead to the formation of unbranched ($P'_2P''_m$) or branched ($P'_{n+2}P''_m.P'''_n$) chains. Simple chains are described by the homologous formula $P_x^{(x+2)}$. It is satisfied by certain phosphanes[14,15] and organic derivatives of di-, tri-, and tetraphosphanes (Mellor[9], p. 912, Baudler et al.[12], and Baudler and Koch[13]). Skeletons comprising two phosphorus atoms [structure (I)] are present in certain phosphorus sulphides (Van Wazer[1], p. 294), in tetraphosphorus trithiodi-iodide[16], in a series of mono- and di-phosphides (Corbridge[10], pp. 17, 18, 62), and certain phosphorus acids (Mellor[9], p. 597). P_3^5 and P_5^7 chains have been found in lanthanum diphosphide[19] [(II) and (III)]:



Rings

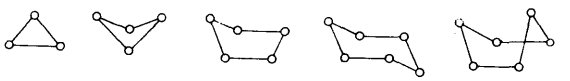
Rings consisting only of doubly-linked phosphorus atoms are described by the formula $P_m^n = P_x^x$ [structures (IV) to (VIII)]. According to the phosphorus stereochemistry, when $m > 3$ the rings are bent. The analogy between

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‡ Skeletons comprising linked quinquevalent phosphorus are less characteristic. They are involved in the structures of the molecules of certain phosphorus acids, for example $H_4P_2O_6$, $H_5P_3O_8$, $H_6P_4O_{10}$, and $H_6P_6O_{12}$, and their salts (Mellor[9], p. 598), as well as the compound $(PO)_4(PPh)_6$ (Corbridge[10], p. 422).

§ The structures of the polyphosphides K_4P_6 and Pb_4P_6 contain planar six-membered P_6^{4-} rings in which the distance between the phosphorus atoms is 2.15 Å, indicating the presence of a non-localised π bond between phosphorus atoms[11].

phosphorus and non-aromatic carbon rings suggests that a six-membered phosphorus ring can exist in the "chair" and "boat" forms [structures (VII) and (VIII)], the former being energetically preferable (Corbridge[10], p. 383):



(IV), P_3^{II} (V), P_4^{II} (VI), P_5^{II} (VII), P_6^{II} (VIII), P_6^{II}

Classification of types of phosphorus skeletons.

Structures of phosphorus skeletons	Homologous formula P_x^y	Polymorphic modifications of elemental phosphorus	Polyphosphorus compounds: phosphanes	poly-phosphides	organo-phosphorus compounds	other compounds	Compounds incorporating groups with similar structures and P–E–P linkages
"Island" structures							
Simple chains	$P'_{n+2}P''_m\cdot P'''_n=P_x^{x+2}$	—	P_xH_{x+2} (x=2—7)	CaP^*, LaP_2, MP_2(M=V, Nb, Ta, Mo, W, Fe, Ru, Os, Rh, Ni, Pt, Si), NiP_3^*, CoP_3^*	P_2R_4, P_3R_5, (R=Ph, Et, CF_3), $M_2P_4R_4$ (M=Li, Na, K; R=Et, Me)	$H_5P_3O_7$, $H_6P_4O_{10}$, $H_4P_2O_4$, $H_4P_2O_5$	$H_4P_2O_7$, $H_6P_3O_{10}$, $H_{n+2}P_nO_{3n+1}$
Rings	$P''_n=P_x^x$	—	P_xH_x (x=3—6)*	—	P_xPh_x (x=4—6) $P_x(CF_3)_x$ (x=4,5)	$(HPO_2)_6$	$(HPO_3)_3$, $(HPO_3)_4$, $H_4P_4O_{10}$
Clusters	$P''_mP'''_n=P_x^{x-n}$ (n-even)	P_4(gas, white phosphorus)	P_xH_{x-2} (x=4—8, 10)*, P_xH_{x-4} (x=6—9)*, P_xH_{x-6} (x=9, 10)*, P_xH_{x-8} (x=10—12)*,	Sr_3P_{14}, Ba_3P_{14}, Na_3P_{11},	$P_{10}Ph_6$, $P_{13}R_5^*$, $P_{14}R_4^*$, $P_7R_3^*$ (R=[$(CH_3)_3$·Si])	—	$P_4O_4S_6$, $P_4O_6S_4$, P_4S_x (x=3, 5, 7, 10), P_4O_x (x=6—11), $H_2P_4O_{11}$, $P_{10}Ph_6R_4$ (R=O, Sn, Ge, Si)
Condensed structures	—	—	$P_{12}H_4^*$, $P_xH_x^*$ (x=7,8)	—	—	—	$H_4P_4O_{12}$
Chain structures							
Simple chains	$P'_nP''_mP'''_n=P_1^1$	—	$P_xH_x^*$	LiP, NaP, tetragonal ZnP_2, monoclinic ZnP_2, PdP_2, monoclinic NiP_2, α-CdP_2, TiP_2, ZrP_2, HfP_2	—	—	—
Ring chains	$P''_\alpha P'''_{2(p+q)}$	—	—	MoP_4, CrP_4, MnP_4, BaP_3	—	—	—
Cluster chains	$P''_\alpha P'''_\beta$	P*(red, amorphous)	—	NaP_7, RbP_7, KP_{15}	—	—	—
Mixed chains	$P''_\alpha P'''_\beta$	—	—	M′M″P_{14} (M′=Zn, Cd, Hg; M″=Pb, Sn)	—	—	—
Layer structures	$P''_\gamma P'''_{2t}$	P*(black, amorphous), P(black, orthorhombic)	—	CaP_3, SrP_3 CdP_4, MgP_4, CuP_2, AgP_2, MP_5(M=La, Ce, Nd, Sm, Gd)	—	—	P_4O^*, orthorhombic P_2O_5, orthorhombic-P_2O_5
Cross-linked structures							
Cross-linked "island" structures		—	—	—	—	—	—

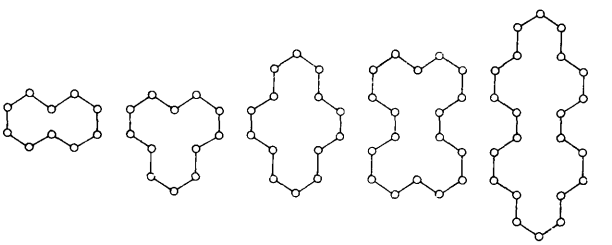
Table (contd.)

Structures of phosphorus skeletons	Homologous formula P_x^y	Polymorphic modifications of elemental phosphorus	Polyphosphorus compounds: phosphanes	poly-phosphides	organo-phosphorus compounds	other compounds	Compounds incorporating groups with similar structures and P–E–P linkages
Cross-linked chains	P''_{m-r-2s}	P(red, crystalline)	—	$LiP_5TlP_8\cdot LaP_7$	—	—	—
Cross-linked layers	$P'''_{n+2r+3s}$		—	—	—	—	—

Notation: l, m, and n represent the amounts of singly-, doubly-, and triply-linked phosphorus atoms in the skeleton respectively; t is the number of clusters and (or) rings joined together in the basic group; p and q are the numbers of P–P bonds and common edges necessary to construct the basic group; k is the number of atoms in the common sides in condensed clusters or rings; r and s are the numbers of $\rangle P-P-P\langle$ and $\rangle P-P\langle$ bridge bonds in the cross-linked skeletons; i are the indices of rings and clusters; j are indices of common sides or edges; $\alpha = \sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j - 2(p+q)$;

$\beta = \sum_{i=1}^{t} n_i + 2(p+q)$; $\gamma = \frac{1}{2}\sum_{i=1}^{t} m_i - 3t$.

Five- and six-membered rings are the fundamental structural elements of the most stable clusters. We may note that cyclic chains and layers formed by the condensation of six-membered rings or derivatives of these rings comprising an even number of phosphorus atoms have been found in many polyphosphides [structures (IX)–(XIII)]. Rings with m = 4–6 are formed in organophosphorus compounds (Mellor[9], p. 913, and Corbridge[10], p. 383) and apparently in phosphanes having the composition P_XH_X (x = 3–6)¶ [15]:



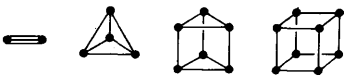
(IX), P_{10}^{II} (X), P_{12}^{II} (XI), P_{14}^{II} (XII), P_{16}^{II} (XIII), P_{22}^{II}

Clusters

The cluster structures consist of convex polyhedra the vertices of which contain triply-linked atoms and the faces are formed by rings comprising three–six phosphorus atoms. The number of faces in the cluster is determined by the number of triply-linked phosphorus atoms n and is equal to $\frac{1}{2}n + 2$. Consequently cluster structures may be made up of P_n''' skeletons, where n is even, consisting of

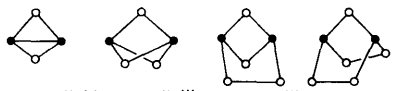
¶ The hypothesis[20] that the phosphanes P_XH_X have a chain structure is less probable. On this hypothesis, the phosphane P_3H_3 should have the structure $H_2P-P=PH$ and chains with a larger number of phosphorus atoms should be described by the formula $P'_2P''_mP'''_2$.

an even number of triply-linked phosphorus atoms [structures (XIV)–(XVII)], the bonds between P''' atoms being ruptured and doubly-linked phosphorus being added at the site of rupture. Each of the initial skeletons is the parent of an individual homologous series.



(XIV), P_2''' (XV), P_4''' (XVI), P_6''' (XVII), P_8'''

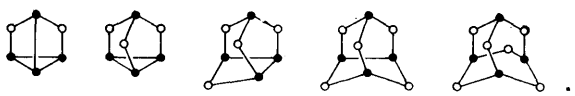
The homologous series originating from the P_2''' skeleton (XIV) is described by the formula $P_m''P_2''' = P_X^{X-2}$ [(XVIII) to (XXI)]. The phosphanes P_XH_{X-2} ($x = 4-8$, 10) satisfy this formula[14].



(XVIII), $P_2''P_2'''$ (XIX), $P_3''P_2'''$ (XX), $P_4''P_2'''$ (XXI), $P_5''P_2'''$

In polyphosphides and organophosphorus compounds clusters of this series have not been found in a free form, but the $P_5''P_2'''$ cluster ("boat" configuration whose raised ends are linked by the seventh phosphorus atom) (XXI) is the fundamental structural element in the lattice of crystalline red phosphorus[21] and many polyphosphides[5,22,23].

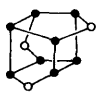
Clusters based on the tetrahedral molecule P_4''' (XV) are described by the formula $P_m''P_X''' = P_X^{X-4}$ [structures (XXII)–(XXIV)]:



(XXII), $P_2''P_4'''$ (XXIII), $P_3''P_4'''$ (XXIV), $P_4''P_4'''$ (XXV), $P_5''P_4'''$ (XXVI), $P_6''P_4'''$

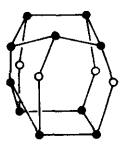
This formula is satisfied by the phosphanes P_6H_2, P_8H_4, P_9H_5, and P_7H_3. The P_7^{3-} cluster (XXIII) has been found in the polyphosphides Ba_3P_{14} and Sr_3P_{14}. We may note that these clusters have the same structures as phosphorus sulphides and oxides.

The homologous series of the P_X^{X-6} and P_X^{X-8} clusters may be constructed similarly on the basis of the trigonal prism P_6''' (XVI) and cube P_8''' (XVII). The formulae of these series are satisfied by the phosphanes P_9H_3, $P_{10}H_4$, $P_{10}H_2$, $P_{11}H_3$, and $P_{12}H_4$.[14] A representative of the homologous series based on the cube is present in the lattice of the polyphosphide Na_3P_{11} (XXVII)[24] and probably in the compound $[(CH_3)Si]_5P_{13}$.[25]



(XXVII), $P_3''P_6'''$

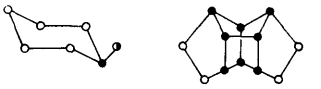
One can imagine clusters consisting of more than eight triply-linked phosphorus atoms which give rise to the homologous series P_X^{X-10}, P_X^{X-12}, etc. For example, the P_{14}^4 cluster in the compound $[(CH_3)Si]_4P_{14}$[25] may be obtained from the P_{10}''' cluster, which consists of a pentagonal prism. The cluster constructed in this way should be represented by formula (XXVIII):



(XXVIII), $P_4''P_{10}'''$

Condensed Structures

Rings containing more than seven phosphorus atoms have not been detected in the structures investigated. The P_8H_8 and P_9H_9 phosphanes have been reported[14,15]. They can be made up of eight- or nine-membered rings, but the formula P_X^X is also satisfied by phosphorus structures (XXIX) having the composition $P_n'P_m''P_n''$ and formed by the addition of singly-linked phosphorus atoms to rings:



(XXIX), $P'P_5''P'''$ (XXX), $P_4''P_6'''$

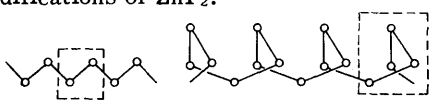
An example of the condensed "island" structure is also the P_{12}^4 cluster (XXX) obtained from two clusters (XXI) when the latter are joined via their common edge and a P–P bond. This cluster is the structural element of the phosphorus skeletons in the crystal lattice of red phosphorus[21] and many polyphosphides[5,22,23].

III. CHAIN STRUCTURES

Chain structures are formed when single phosphorus atoms (simple chains), rings (ring chains), and clusters (cluster chains) are joined together to form infinitely long chains. Ordered chains have been found in the crystal lattices of many polyphosphides[5] and in the structure of crystalline red phosphorus[21].

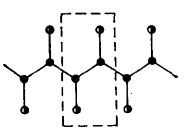
Simple Chains

The consecutive combination of phosphorus atoms can lead to the formation of zigzag or helicoidal chains described by the formula P_X^X (Schnering[5] and Corbridge[10], p.40). Zigzag chains (XXXI) are present in the crystal lattices of titanium, hafnium, zirconium, and palladium diphosphides (Corbridge[10], p.40), helicoidal chains (XXXII) have been found in the LiP,[26] NaP,[26] and α-CdP_2[27] lattices and in the lattices of the tetragonal and monoclinic modifications of ZnP_2.[28,29]



(XXXI), P_2'' (XXXII), P_4''

One may postulate the formation of branched phosphorus chains having the general formula $P_n'P_m''P_n''' = P_1^1$, for example, with $m = 0$ and $n = 1$ as in structure (XXXIII):

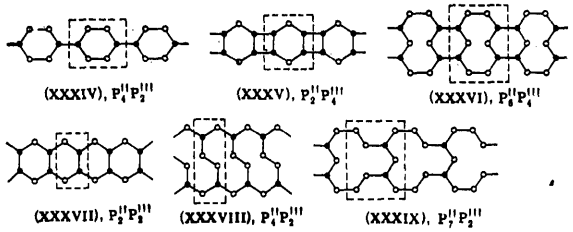


(XXXIII), $P_2'P_2'''$

Multiring Chains

When identical or different rings are joined together in an ordered or non-ordered manner, multiring chains may be formed. Such chains are either independent structural elements or form part of more complex phosphorus structures.

On forming chains, the rings can be joined by one [as in (XXXIV)] or two [as in (XXXV) and (XXXVI)] bonds or by a common side [as in (XXXVII)–(XXXIX)]:



(XXXIV), $P_4''P_2'''$ (XXXV), $P_2''P_4'''$ (XXXVI), $P_6''P_4'''$

(XXXVII), $P_2''P_3'''$ (XXXVIII), $P_4''P_2'''$ (XXXIX), $P_7''P_2'''$

On formation of each bond between the rings, two doubly-linked phosphorus atoms become triply-linked. In order to form a common side, it is necessary to remove k atoms from two rings; the common side then consists of two triply-linked and $k-2$ doubly-linked phosphorus atoms. In the general case the basic group of such an infinite ordered chain, made up of t rings, is described by the formula $P_x^{x-2(p+q)}$, where $x = \sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j$, m_i is the number of phosphorus atoms in each initial ring, p the number of new P–P bonds formed when the rings are linked to one another, and q the number of common sides, each of which contain k_j phosphorus atoms.

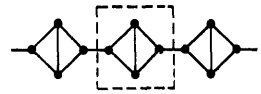
The most typical should be the simplest cases where the chain is made up of identical rings, linked to one another in the same manner. In this case $i = 1$ and, for singly-linked rings ($p = 1$, $q = 0$), we obtain the homologous formula P_x^{x-2} ($x = m$); for doubly-linked rings ($p = 2$, $q = 0$), we have the formula P_x^{x-4} ($x = m$); for rings linked by a common side ($p = 0$, $q = 1$), we have the formula P_x^{x-2} ($x = m - k$). Infinite chains made up of singly-linked six-membered rings in the chair form (XXXIV) are the structural elements of the BaP_3 crystal lattice [30]. The multiring chains (XXXVII) are components of the phosphorus structure in lithium polyphosphide LiP_5. [31]

Cluster Chains

Like rings, clusters can be joined together to form chains via one or two P–P bonds or by the formation of common edges. The linking of clusters by three P–P bonds or by the formation of a common face is unlikely in view of steric hindrance. There is also a possibility that clusters are linked together with formation of both a P–P bond and a common edge [as in (XXX)]. The basic group in an infinite ordered cluster chain consisting of t clusters $P_{m_i}''P_{n_i}'''$, joined by p P–P bonds, and forming q common sides is described by the formula P_x^y, where

$$x = \sum_i (m_i + n_i) - \sum_{j=1}^{q} k_j, \quad y = \sum_i m_i - 2(p+q) - \sum_{j=1}^{q} k_j.$$

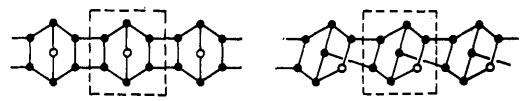
In order that the clusters can be connected to form chains, they must contain at least two doubly-linked phosphorus atoms [see (XVIII)–(XXVIII)]. The basic group of a chain consisting of identical clusters $P_m''P_n'''$, linked to one another by a single P–P bond, is described by the formula $P_{m+n}^{m-2} = P_x^{x-n-2}$. Such a chain (XL), obtained by joining together singly-linked clusters (XVIII), can be seen in the structure of amorphous red phosphorus proposed by Pauling and Simonetta [32].



(XL), P_4'''

Clusters joined together by two bonds should have at least four doubly-linked phosphorus atoms. The clusters (XX), (XXI), (XXII), and (XXX) may be of this kind. The formula of the basic group of the chain consisting of identical clusters is $P_{m+n}^{m-4} = P_x^{x-n-4}$.

Structures (XLI) and (XLII) consist of chains comprising the $P_5''P_2'''$ cluster (XXI):



(XLI), $P''P_6'''$ (XLII), $P''P_6'''$

Such chains occur in the crystal lattices of the polyphosphides RbP_7 (XLI) and LiP_7, NaP_7 (XLII). [5,31]

Clusters joined together with formation of common sides must have at least two edges containing not less than two P″ atoms. This condition is satisfied only by clusters (XXI) and (XXX). Evidently these clusters are in fact the most convenient structural elements of the cluster chains. The structures of crystalline red phosphorus (XLIII) [21] and a number of polyphosphides, for example KP_{15}^{33} (XLIV), are constructed on their basis:



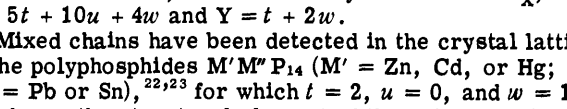
(XLIII), $P_2''P_{10}'''$ (XLIV), $P''P_{14}'''$

If the chain is formed from t clusters of type (XXI) by joining together the latter with formation of p new P–P bonds and q common sides, the formula of the basic group becomes $P_{7t-2q}^{5t-2p-4q} = P_x^{x-2(p+t+q)}$ (for example, in the KP_{15} structure we have $t = 3$, $p = 1$, and $q = 3$).

Mixed Chains

Infinite chains can also be formed by joining together clusters and rings. The formation of mixed chains from P_6^6 [(VII) and (VIII)] and the clusters P_7^5 (XXI) and P_{12}^4 (XXX), joined by their common sides, is most probable. The basic group, consisting of w rings P_6^6, t clusters P_7^5, and U clusters P_{12}^4, is described by the formula P_X^Y, where $x = 5t + 10u + 4w$ and $Y = t + 2w$.

Mixed chains have been detected in the crystal lattices of the polyphosphides $M'M''P_{14}$ (M′ = Zn, Cd, or Hg; M″ = Pb or Sn), [22,23] for which $t = 2$, $u = 0$, and $w = 1$ and which are the structural element of the polyphosphide [34] TlP_5 ($t = 1$, $u = 0$, $w = 1$) [see (XLV) and (XLVI)]:

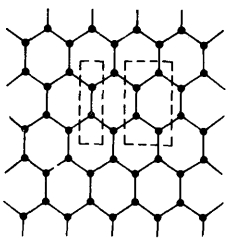


(XLV), $P_4''P_{10}'''$ (XLVI), $P_3''P_6'''$

IV. LAYER STRUCTURES

Regular layer structures can be made up by joining together ring chains via P–P bonds or by the formation of common sides. In the crystal lattice of black phosphorus and many polyphosphides layer structures based on the rings (VII) and (IX)–(XIII) have been detected[5,35]. The formation of layer structures from cluster chains is unlikely for steric reasons.

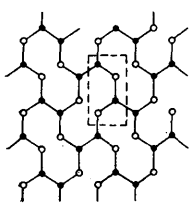
Suppose that a layer is made up of identical chains whose basic group is described by the formula $P''_mP'''_n$. If on formation of the layer two basic groups are joined by p bonds P–P and give rise to k common atoms of which j atoms are triply-linked, the formula of the basic group is P_x^y, where $x = m + n - k$ and $y = m - 2p - j$.



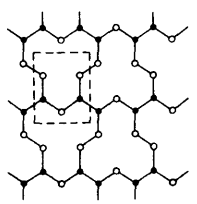
(XLVII), $P_2'''P_4'''$

For example, the structure of the layer in black phosphorus (XLVII) can be represented as a result of the linking of the chains (XXXVII) by P–P bonds (in this case $m = 2$, $n = 2$, $p = 1$, and $k = j = 0$) or by the formation of common sides ($m = 2$, $n = 2$, $p = 0$, $k = j = 2$). The same structure can be made up of the chains (XXXIV) by linking them via P–P bonds ($m = 4$, $n = 2$, $p = 2$, $k = j = 0$) or via common sides ($m = 4$, $n = 2$, $k = j = 4$).

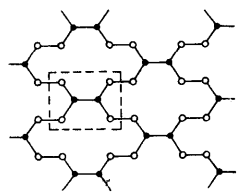
It is simpler to describe layer structures as a result of the joining together of rings of one or more types. It is readily seen that, when the layer is made up of identical rings P''_m, its basic group consists of $\frac{1}{2}(m - 2)$ phosphorus atoms, of which two are triply linked, i.e. the formula of the basic group is P_x^{x-2}, where $x = \frac{1}{2}(m - 2)$. Such layers can be made up only of rings with an even number of phosphorus atoms [the structures of black phosphorus (XLVII) and the polyphosphides CuP_2, AgP_2, CdP_4,[36] MgP_4 [37,38] (XLVIII), LnP_5 [39,40] (XLIX), and CaP_3 (L) [41]].



(XLVIII), $P_2''P_2'''$

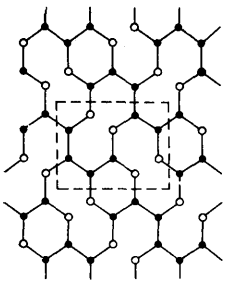


(XLIX), $P_3''P_2'''$

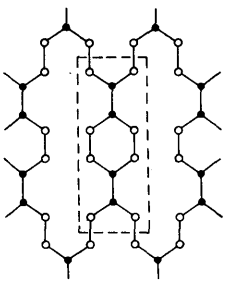


(L), $P_4''P_2'''$

If the layer consists of t rings of type P''_{m_i}, the basic group contains $x = \frac{1}{2}\sum_{i=1}^{t}(m_i - 2) = \frac{1}{2}\sum_{i=1}^{t} m_i - t$ phosphorus atoms, of which $2t$ are triply-linked. The formula of the basic group is P_x^{x-2t}. Examples of layers formed by the condensation of several rings are (LI) ($m_1 = 10$, $m_2 = 10$, $m_3 = 6$) and (LII) ($m_1 = 22$, $m_2 = 6$); the latter structure arises in the crystal lattice of the polyphosphide SrP_3.[40]



(LI), $P_4''P_6'''$



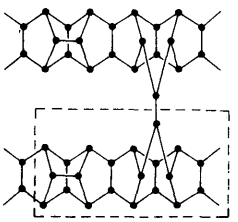
(LII), $P_8''P_4'''$

V. CROSS-LINKED STRUCTURES

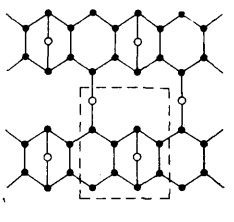
Elementary phosphorus skeletons can be joined together into more complex entities not only by simple connection but also by cross-linking via bridging doubly- or triply-linked phosphorus atoms. Cross-linked phosphorus structures have been found in the crystal lattices of red phosphorus [21] and certain polyphosphides [5,31,34].

The following variants of cross-linked structures may be postulated: chains, layers, and skeletal structures obtained by the cross-linking of rings or clusters; layers and skeletal structures formed from cross-linked chains; skeletal structures made up of cross-linked layers. However, only layer and skeletal structures obtained by the cross-linking of chains have been found in the crystals investigated hitherto.

The cross-linked chains (XLVI) form phosphorus layers in the crystal lattice of TlP_5 [34] (LIII). In the structure of crystalline red phosphorus the chains (XLIII) are linked by bridges comprising a pair of P''' atoms [see (LIV)] with formation of a double layer:

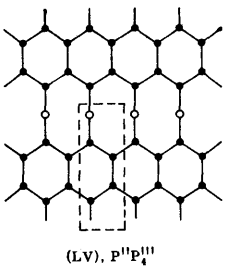


(LIII), P_{21}'''



(LIV), P_2'', P_8'''

The cross-linking of the chains leads to the formation of skeletal structures made up of phosphorus atoms in the crystal lattices of LiP_5 [31] and LaP_7.[42] The projection of the former onto the plane in which the parallel chains are located is of the form



(LV), $P''P_4'''$

The formation of a skeleton in these structures is due to the fact that the bridging phosphorus atoms link together chains located in different planes.

In cross-linking by bridging doubly linked phosphorus atoms $\rangle P-P-P\langle$ two doubly linked phosphorus atoms become triply-linked for each cross-linked bond and a further doubly-linked atom is added. Therefore, if the basic group which was described by the formula $P''_mP'''_n$. before cross-linking is joined to another similar group by r bridge bonds, the formula of the basic group in the cross-linked structure is $P''_{m-r}P'''_{n+2r} = P^y_x$, where $x = m + n + r$ and $y = m - r$. For example, when chains (XXXVII) of the type $P''_2P'''_2$ are cross-linked by bridge bonds (one bond per basic group), we have $m = 2$, $n = 2$, and $r = 1$, i.e. the formula of the basic group in the cross-linked structure is $P''P'''_4 = P^1_5$ (LV).

In cross-linking by triply linked atoms $\rangle P-P\langle$ each bridging atom is connected to two doubly-linked atoms, converting them into triply-linked atoms. The formula of the basic group after cross-linking is therefore $P''_{m-2s}P'''_{n+3s}$, where s is the number of bridge bonds. For example, cross-linking of the chains P^1_{20} (XLIII) yields the cross-linked structure (LIV) with the basic group P'''_{21}.

VI. CONCLUSION

Using the procedures described above, it is possible to construct a very large number of phosphorus skeletons, including some which have not been considered in this review. It therefore becomes possible to predict the structures of skeletons in polyphosphorus compounds of known composition. As an example, the Appendix presents the development of various procedures for the construction of phosphorus skeletons having the composition P^1_2, the most accurate of which (from our point of view) are then selected. Such phosphorus skeletons should be present in the phosphorus hydride $(P_2H)_x$ and in the polyphosphides having the general formula MP_{2n} (n is the valence of the metal).

Since the same formula corresponds to a whole series of structures, additional information about the properties of the compound is required for an unambiguous selection [6]. Consider an example. The preparation of the solid phosphorus hydride $(PH)_x$ has been reported [9]. Since this compound is resistant to acids and alkalis and decomposes *in vacuo* only at 400°C, it is logical to suppose that it has a polymeric structure. The formula P^1_1 is satisfied only by simple chains and rings, so that one can claim that the phosphorus hydride $(PH)_x$ contains either infinite branched or unbranched phosphorus chains or structures made up of condensed rings formed by a large number of phosphorus atoms, as happens in catenanes [43]; the first hypothesis appears to be more likely.

A greater abundance of comparatively simple skeletons consisting of a small number of structural elements is to be expected for binary compounds of phosphorus with electropositive elements or radicals. The skeletons in polyphosphorus compounds with several different elements or radicals, particularly when these are characterised by different valences, should have a more complex structure.

The ability of phosphorus to form different structures corresponding to the same formula of the basic group reflects the unusual isomerism of phosphorus skeletons. On the basis of this property, one may postulate the possibility of the polymorphism of many polyphosphorus compounds, which may be caused only by changes in the packing of atoms in the unit cell without an alteration of the structure of the phosphorus skeleton (tetragonal [28] and monoclinic [29] modifications of ZnP_2) or may be a consequence of a change in the skeleton [elemental phosphorus and cubic (Corbridge [10], p. 429) and monoclinic [44] modifications of NiP_2].

In the present review we confined ourselves to an examination of regular chain, layer, and three-dimensional structures which are usually present in the crystalline phases. If a statistical distribution of the initial elements in infinite phosphorus structure is postulated, one may investigate different variants of the structures of amorphous and vitreous phases, which are common in the chemistry of phosphorus.

The principles of the construction of phosphorus skeletons described are applicable, as shown above, also to the construction of neutral phosphorus structures consisting solely of triply-linked phosphorus atoms. This makes it possible to build up the probable configurations of polymorphic modifications of elemental phosphorus which have not yet been investigated and which have been mentioned in a number of publications [9,10].

On the basis of the wide variety of structures of phosphorus skeletons, one may postulate the existence of a very large number of different polyphosphorus compounds, since experience gained in the development of chemistry indicates a high reliability of the predictions of the structures of compounds on the basis of the classical theory of valence [45]. In terms of this ability to form polyatomic compounds, phosphorus is inferior only to carbon and possibly to boron [46]. In fact, if the element–element bond energy and the number of covalent bonds are adopted as criteria of the ability to form polyatomic compounds, then, among elements forming more than two bonds, carbon, boron, and phosphorus give rise to the most stable bonds. The smaller number of polyphosphorus compounds compared with carbon compounds is caused both by the tervalence of phosphorus (in contrast to the quadrivalence of carbon) and the smaller energy of the P–P covalent bond (53 kcal mole^{-1}) compared with the energy of the aliphatic C–C bond (83 kcal mole^{-1}). [47] The lower electronegativity of phosphorus and the presence of a lone electron pair and of vacant 3d orbitals in a three-coordinated phosphorus atom lead to a greater reactivity of phosphorus compounds compared with the analogous carbon compounds, which creates definite experimental difficulties.

Homologous series are common in organic chemistry, while in the chemistry of polyphosphorus compounds homologous matrices, consisting of families of homologous series, are abundant. It may turn out that some of the homologous series are represented by a small number of members or even only one member, but one can also encounter skeletons with a similar structure belonging to different homologous series but described by the common formula of the homologous matrix.

The extremely wide variety of structures of polymeric phosphorus molecules noted above, compared with carbon, is associated with the different structures of the two elements.

Rigid tetrahedral sp^3 bonds with a high deformation energy and valence angles differing little from tetrahedral values are characteristic of saturated carbon compounds.

On the other hand, the pyramidal p^5 phosphorus bonds are readily deformed†, which leads to the wide variety of the existing phosphorus skeletons. The tervalence of the phosphorus atom is responsible for the relatively greater abundance of clusters and cluster structures than in the case of carbon. Thus the role of the cluster (XXI) in building up the phosphorus chains has already been noted. The stability of such a cluster is due to the fact that the valence angle in the P–P–P linkage is ~100°. For carbon, which has a greater valence angle, the formation of this type of cluster involves the appearance of strained bonds and carbon compounds involving such a cluster are not typical, although they do exist[8].

The above analysis of the structure of phosphorus skeletons in various polyphosphorus compounds demonstrated, as might have been expected, the existence of homologous series and homologous matrices for the description of which it is sufficient to have a small number of fundamental rules, which in certain cases differ from the rules of organic chemistry. This emphasises yet again the characteristic features of the chemistry of phosphorus and the desirability of separating it as an individual chemical discipline with its own rules governing the description of compounds and the reactions involving them and an individual approach to problems of the specific synthesis of such compounds‡.

VII. APPENDIX (DETERMINATION OF THE STRUCTURES OF P_2^1 PHOSPHORUS SKELETONS)

The P_2^1 phosphorus skeleton is described by the formula $P_l'P_m''P_n'''$ in which $m = n - 3l$. The most typical skeletons do not contain singly-linked phosphorus atoms ($l = 0$) and correspond to the condition $m = n$. We shall confine ourselves to an examination of "island", chain, and layer structures formed by such skeletons.

"Island" Structures

Only $P_2''P_2'''$ (XVIII), $P_4''P_4'''$ (XXIV), $P_6''P_6'''$, etc. clusters as well as condensed structures for which $m = n$ satisfy the formula P_2^1. Since $m = \sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j - 2(p+q)$ and $n = \sum_{i=1}^{t} n_i + 2(p+q)$, the relation between the parameters characterising such structures is defined by the equation $\sum_{i=1}^{t} (m_i - n_i) - \sum_{j=1}^{q} k_j = 4(p+q)$. For example, when the condensed cluster is formed from two identical clusters linked by a single P–P bond, we have $t = 2$, $k = 0$, $p = 1$, $q = 0$, and $m_1 - n_1 = 2$. Consequently $P_4''P_2'''$, $P_6''P_4'''$, etc. clusters can be combined into an "island" structure in the way described.

The formation of the following "island" structures is most probable: the $P_4''P_4'''$ cluster all sides of which consist of five-membered rings or the cluster (XXIV) whose sides consist of two five-membered rings, one six-membered ring, and one four-membered ring.

Among condensed structures, the formation of the $P_6''P_6'''$ cluster, obtained when two $P_5''P_2'''$ (XXI) clusters combine with establishment of a common side comprising two atoms, is most probable.

Chain Structures

Multiring, cluster, or mixed chains can correspond to the formula P_2^1. The condition $m = n$ for multiring chains may be formulated as follows: $\sum_{i=1}^{t} m_i - \sum_{j=1}^{q} k_j = 4(p+q)$. For chains made up of identical rings ($t = 1$), this formula assumes the form $m_1 - k_1 = 4(p+q)$. Consequently a singly-linked chain ($p = 1$, $q = 0$, $k = 0$) consists of four-membered rings; a doubly-linked chain ($p = 2$, $q = 0$, $k = 0$) consists of eight-membered rings; a chain formed by the linking together of rings consisting of m_1 phosphorus atoms and involving the establishment of a common side comprising k_1 atoms ($p = 0$, $q = 0$) is described by the formula $m_1 = k_1 + 4$. If $k_1 = 2$ and $m_1 = 6$, we obtain the chain (XXXVII). Chains with $k_1 > 2$ are unlikely for steric reasons.

Cluster and mixed P_2^1 chains are described by the equation $\sum_{i=1}^{t} (m_i - n_i) - \sum_{j=1}^{q} k_j = 4(p+q)$. Analysis shows that the formation of such chains with a simple structure is impossible.

Layer Structures

The condition $m = n$ assumes the following form for layers whose basic group consist of t rings: $m_1 - k_1 = 4(p+q)$. The layer formed by the condensation of identical rings should therefore incorporate P_{10}'' rings (XLVIII). The layer obtained by the condensation of P_{m_1}'' and P_{m_2}'' rings of different kinds must satisfy the condition $m_1 + m_2 = 20$, i.e. it can be formed only for $m_1 = 6$ (VII) and $m_2 = 14$ (XI).

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† In the structure of crystalline red phosphorus the valence angles between bonds vary from 84.5° to 115.9° and the distance between linked phosphorus atoms varies from 2178 to 2.299 Å,[22] although the average valence angle (101°) and the P–P distance (2.22 Å) are close to the optimum values observed in the structure of the most stable modification—black phosphorus[27].

‡ See also the recently published review by H.G. Schnering (in "Homoatomic Ring Chain Macromolecules of Main-group Elements", Elsevier, Amsterdam, 1977) in which new structural data, not included in this review, are presented.

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The Present State of the Quantitative Theory of Polycondensation Processes

S.I.Kuchanov and E.B.Brun

The computational and theoretical studies in the field of homogeneous polycondensation are subjected to a critical analysis on the basis of the universal classification of the kinetic and thermodynamic models used in this field. The limits of the applicability of the models are discussed from the standpoint of the physicochemical characteristics of the processes which they describe and the parameters calculated on their basis are compared with the corresponding experimental data. The fundamental problems awaiting solution by the quantitative theory of polycondensation in the present stage of its development are formulated.
The bibliography includes 297 references

CONTENTS

I. Introduction 162
II. Linear polycondensation 165
III. Branched polycondensation 172

I. INTRODUCTION

The polycondensation method for the synthesis of polymers is at present one of the most widely used procedures for the formation of synthetic high-molecular-weight products. The extensive scope of this method is associated with the wide variety of monomers employed as well as the chemical reactions leading to the formation of macromolecules. In view of the practical importance of polycondensation it has been the subject of an enormous number of experimental studies. Here mention should be made of the great contribution made by V. V. Korshak and his School to the development of ideas about polycondensation processes. These studies made it possible to understand many important features of polycondensation and to obtain new polymers with valuable practical properties.

An enormous amount of experimental data on polycondensation has now accumulated. They have been surveyed and arranged systematically in monographs devoted both to individual important classes of polycondensation polymers[1-5] and to general characteristics of polycondensation[6-10]. However, in all these monographs, except Flory's familiar book[11], mainly experimental data are quoted and very little space is devoted to the quantitative theory and computational studies. At the same time, in planning industrial manufacturing processes one of the most important tasks is that of selecting the optimum conditions for polycondensation processes. The successful solution of this problem requires a well developed quantitative theory of such processes[12], which would make it possible to devise for them adequate mathematical models and to seek with the aid of a computer the optimum technological polycondensation régimes in terms of such models.

The present review presents a critical analysis of published computational and theoretical studies devoted to homogeneous polycondensation processes. Attention has been concentrated on the discussion of the initial postulates of the theory, the illustration of the possibilities of various computational methods, and the general problems of the modern quantitative polycondensation theory. Certain results arising from the theory of heterophase polycondensation are quoted in the review of Sokolov and Nikonov[13].

For a detailed statistical description of the products of linear homopolycondensation, it is sufficient to determine their molecular weight distribution (MWD). If cyclisation reactions proceed to an appreciable extent during the process, it is necessary to find also the MWD of the cyclic molecules. The copolymer molecules differ not only in the degree of polymerisation (size) but also in the fractions of units of different types (composition). The inhomogeneity of the copolycondensation products will therefore be described in terms of a size–composition distribution function (SCD). Furthermore, copolymer molecules having the same size and composition can have completely different microstructures characterised by the way in which the units are distributed in the chain. On passing from linear to branched polymers, it is necessary to take into account in their statistical description the fact that, apart from the above characteristics, macromolecules differ also in their steric configurations, particularly in the number and lengths of branches and intermodal chains, although for many practical purposes there is no need to distinguish all possible isomers in the description of the process.

The statistical characteristics enumerated above determine the primary, i.e. the configurational, structure of macromolecules which carries definite information about their possible conformations and secondary supermolecular structures and hence also about the physicochemical properties of polymers. Thus the main task of the quantitative polycondensation theory is the establishment of computational relations corresponding to the statistical parameters of the primary structure of the polymeric specimen as a function of the composition of the initial monomeric mixture and thermodynamic or kinetic parameters, i.e. as a function of the equilibrium constants or rate constants for reactions occurring during the synthesis of the polymer. The solution of this problem will permit an approach on a sound scientific basis towards the selection of the optimum polycondensation conditions in order to obtain polymers with a specified set of practical properties.

In the course of polycondensation there is a possibility of the simultaneous occurrence of different types of elementary reactions. The main one of these is chain

propagation—the interaction of two functional groups in different molecules to form the corresponding linkage between them, which will henceforth be referred to as the "intramolecular bond". This involves the joining together of two reacting molecules of monomers, oligomers, or polymers into a single entity which is frequently (but not necessarily) accompanied by the liberation of a molecule of a low-molecular-weight product. A common feature of polycondensation is [14] that during its course any two molecules of the initial or intermediate product in the reaction mixture, containing interacting functional groups, can be involved in a condensation reaction with one another. The reverse reaction in relation to chain propagation is chain degradation. For fairly high equilibrium constants k corresponding to this pair of elementary reactions, degradation in the course of polycondensation can nevertheless be neglected and their polycondensation can be regarded as an irreversible process. On the other hand, if k is small, the reversibility of polycondensation becomes significant. Whereas irreversible polycondensation is always a non-equilibrium process, reversible polycondensation can proceed under both equilibrium and non-equilibrium conditions. In order to achieve the equilibrium régime, it is necessary to remove the low-molecular-weight side product from the reaction zone at a fairly low rate, so that at each instant the system is in a state of thermodynamic equilibrium corresponding to the current concentration of the side product. The rate of this removal from the reaction zone evidently determines the overall rate of such equilibrium polycondensation. On the other hand, if the rate of removal of the side product is comparable to the rate of its formation in the condensation reaction, then reversible polycondensation will proceed in a non-equilibrium régime.

Apart from the growth and degradation of polymeric chains, elementary reactions involving interchain exchange, chain termination and intramolecular cyclisation are possible in the course of polycondensation. Without influencing the number-average degree of polymerisation, interchain exchange reactions can to a large extent determine the form of the MWD and the SCD for the polymer. Exchange reactions may be of two types. The elementary step in the first type involves the interaction of the terminal functional groups with an intermolecular bond, while in the second type it involves the interaction of two such bonds with one another. Apart from terminal functional groups (for example hydroxy-, carboxy-, or amino-groups), in calculations on reversible polycondensation it is necessary to treat intramolecular bonds [for example, ester(ether) or amide bonds] as "internal" functional groups, because they are involved in elementary degradation and interchain exchange reactions. Chain termination reactions in polycondensation, which consists in chemical deactivation of terminal functional groups, frequently takes place as a result of the interaction of the latter with monofunctional compounds, which are either specially introduced or are present in the system as impurities. In intramolecular cyclisation both reacting functional groups belong to the same molecule so that this type of reaction, which increases the degree of conversion of the group, does not lead to the growth of the molecular weight of the polymer†. In practical calculations there is usually no need to take into account all the elementary reactions, since, under the conditions of a specific process, many of them take place to such an insignificant extent that they can be neglected in setting up a kinetic scheme.

In the calculation of the statistical characteristics of the primary structure of polycondensation products two approaches are used: kinetic and statistical. The first consists in setting up and solving material balance equations for the concentrations of all types of molecules participating in the given process. In the second process the fractions of molecules with specified configurations, among others in reaction mixture, are calculated. These fractions are identified with the probability that a molecule selected at random has the corresponding configuration. There exist various versions of the statistical approach to the calculations of the above probabilities for molecules and even within the same class of processes it is possible to use several of them simultaneously. In the most convenient approach each macromolecule is represented as an individual occurrence of a definite random process involving conventional motion along the polymer chain and the probability of such occurrence is calculated with the aid of the theory of the corresponding process.

The statistical approach to calculations on polycondensation processes was first proposed by Flory as early as the end of the 1930s [11] and has found the widest applications in the quantitative description of many polymers, both linear and branched. The principal advantage of the statistical approach is that it makes it possible to describe exhaustively and at the same time comparatively simply the detailed configurational structure of macromolecules in terms of several probability parameters. However, the problem of the selection of the type of random process for a description of the products of a specific polycondensation system cannot be solved, in principle, within the framework of the statistical method alone. An answer is provided by the kinetic approach, which makes it possible to express simultaneously the corresponding probability parameters of the random process in terms of kinetic constants, reactant concentrations, and other measurable quantities. In order to prove rigorously the applicability of a particular modification of the statistical approach to the description of the primary configurational structure of the products of equilibrium polycondensation, the general principles of statistical physics and chemical thermodynamics, particularly the principle of detailed balancing, are used. Thus at equilibrium the probability of observing an arbitrary molecule in the system is determined by the free energies of formation of all its intramolecular bonds and, according to the principle of detailed balancing, is independent of the order in which the bonds appear, i.e. of the previous history of the system. On the basis of general thermodynamic relations, it is possible to express the free energy of formation of intramolecular bonds in terms of the equilibrium constants of the elementary reactions corresponding to the stoichiometric scheme for the given process. This makes it possible to determine in terms of these quantities the probability parameters used in the statistical approach.

In the course of the development of a quantitative theory of polycondensation two stages may be traced. In the first stage, which originated from Flory's fundamental work [11], only systems which we shall henceforth call ideal are considered. They do not involve intramolecular reactions and Flory's principle applies to the intermolecular reactions. According to this fundamental principle, the activity of any functional group of a particular type in each elementary reaction is the same regardless of which molecule the given group belongs to and in which part of the

†In the present review we are not considering polycondensation processes where only functional groups adjoining the chain can take part in the cyclisation reaction.

molecule it is located. The model of ideal polycondensation systems, to the development of which most published theoretical studies have been devoted, permitted the calculation by various methods of the necessary statistical characteristics of the products of the most general polycondensation processes with participation of many monomers of arbitrary functionality and with functional groups of various types. The problem of devising a theory of ideal polycondensation can now be regarded as largely solved[12]. The next stage consisted in a quantitative description of non-ideal systems. The attempts at calculations on such systems are usually associated with the overcoming of fundamental difficulties and the wide variety of factors tending to cause a departure from ideality precludes the use of a particular single approach. This stage of the development of the theory is therefore still far from complete.

We shall note the physical principles underlying the initial postulates of the model of ideal polycondensation systems and shall point out certain causes which may lead to the breakdown of these postulates. In the first place one should note that polycondensation reactions are comparatively slow and therefore occur under liquid phase conditions in such a way that their rate is not as a rule limited by diffusion factors. Intermolecular reactions are of second order, while intramolecular reactions are of first order, which leads to an increase of the proportion of the latter as the reaction mixture is diluted by an inert solvent. It is easy to achieve a condition where cyclisation reactions may be neglected in the description of the process kinetics. The probabilities, per unit time, that an arbitrary selected functional group of a macromolecule is involved in competing condensation reactions of the intermolecular and intramolecular type are respectively kC and k', where k and k' are the rate constants for bimolecular and unimolecular reactions and C is the concentration of the functional groups in the system. The quantity k' is proportional to the number of conformations of the initial molecule for which another group of this molecule is in the immediate vicinity of the selected group, i.e. is proportional to the effective local concentration c, which all the remaining groups of the molecule set up near the selected group as a result of the conformational rearrangements of the molecule. Since conformational equilibrium is assumed in the system, c is identical with the concentration of the corresponding conformers. If the functional groups in the molecule are separated by a fairly large number of intramolecular bonds, the proportionality coefficient between k' and c is equal to k, because the probabilities of the elementary step in the intramolecular and intermolecular reactions are in this case identical. Consequently $k' \ll kc$ and it is legitimate to neglect intramolecular reactions when $c \ll C$. The quantity C diminishes in proportion to the dilution of the system and c is determined by the configuration and segmental mobility (flexibility) of the polymer chains and is almost independent of the degree of dilution, although it may change on passing from one solvent to another. If it is supposed that the rates of the reverse reactions are independent of the conformational structure of the molecule, the foregoing statements concerning the rate constants for condensation reactions are fully applicable also to the corresponding equilibrium constants k' and k. In particular, if the functional groups involved in the reaction are separated by a large number of intramolecular bonds, the ratio k'/k is equal to the effective concentration c. At equilibrium the ratio c/C determines the contribution to the free energy change of the macromolecule in a given intramolecular reaction associated with the decrease in its course of the number of possible conformations of this molecule. Consequently c is unambiguously determined by the conformational entropy of the macromolecule and can be calculated by thermodynamic methods.

The possible causes of the deviations from Flory's principle can be divided into two classes, by analogy with the conformational properties of macromolecules: the short- and long-range effects. The former include the so called substitution effects associated with steric, inductive, or other types of influence of functional groups which have reacted on the activities of the neighbouring functional groups which have not. One speaks of a first-order substitution effect if the reactivity of the group depends on the state of the functional group only in the same monomer unit. Sometimes it is necessary to take into account also the possibility of higher-order substitution effects where the reactivity of the given group is influenced by the state of the groups in neighbouring units. Long-range order effects are determined by the possible influence of the solvent on the steric conformational structure of macromolecules and hence on the activity of the functional groups contained in them. For example, on passing from "good" to "poor" solvents, there is a possibility of the contraction of the reacting macromolecules accompanied by a reduction of the accessibility of the functional groups and actually resulting in the limit in the complete loss of reactivity by these groups owing to their intramolecular "protection". Such long-range order effects, where the accessibility of each individual group for reaction with other groups is determined by the conformational-configurational structure of the entire macromolecule, are significantly more difficult to take into account in the polycondensation theory than the short-range order effects. In the latter case calculations on polycondensation systems taking into account the substitution effect are carried out using the generalised Flory principle[12], according to which the activity of any functional group in the molecule can depend only on the microstructure of the neighbouring sections of the polymer chain and varies during the process owing to the changes in its microstructure associated with the reaction of neighbouring groups.

There is at present virtually no quantitative theory of polycondensation in which long-range order effects are rigorously taken into account. The difficulties in devising such a theory are due to the inapplicability in this instance of the Flory principle even in its generalised formulation. Such a theory requires the consideration of the conformational-configurational statistics of the reacting molecules. In contrast to intermolecular reactions, calculations on intramolecular reactions within the framework of the theory taking into account only the short-range order effect cannot be made at all. This is reasonable, because the interaction of any pair of functional groups within a single molecule depends significantly on their relative positions in the molecule and possibly on the choice of equilibrium conformations of the molecule, which determine the probability of the steric approach of the given groups to a distance necessary for the chemical reaction step.

An important property of ideal polycondensation systems, associated with the random nature of the reactions occurring in them, should be noted. Any statistical characteristics of the products of ideal polycondensation are independent at any instant of the previous history of the system, i.e. of whether the process takes place under equilibrium or non-equilibrium conditions, whether

degradative or exchange reactions occur, or whether the process is fully irreversible. They are fully determined by the concentrations of the terminal functional groups and the intramolecular bonds of each type at a given instant. In calculations on such systems by any statistical method this makes it possible to choose the numbers of functional groups and bonds of each type in an arbitrary molecule as parameters which unambiguously specify its probability. Thus in non-equilibrium processes the state of the system is independent (as at equilibrium) of its previous history, is associated with the ideality of these processes, and may break down on deviation from the latter; the probability of the appearance of a particular molecule in the absence of equilibrium can then depend also on the order in which its bonds have been formed. In the description by the statistical method of products of non-ideal polycondensation processes in the absence of equilibrium it is therefore always necessary to test the method for the adequacy of the chosen model by means of the corresponding kinetic equations.

Next we shall denote various monomers by a sequence of letters, the first of which (R,S,...) corresponds to the monomer unit and each of the latter (A, B,...) corresponds to a definite type of functional group in the monomer. If the monomer contains several identical groups, their number will be designated by a superscript to the corresponding letter.

II. LINEAR POLYCONDENSATION

In order to obtain macromolecules with a linear structure, bifunctional monomers are used. Depending on their number and type, homopolycondensation, heteropolycondensation, and copolycondensation are distinguished. The products of the first two processes are homopolymers, the elementary units of which consist of one or two monomeric units respectively, while the products of the third process are copolymers whose macromolecules differ in size, composition, and microstructure within the limits of a single specimen. Examples of homopolycondensation are provided by processes involving the formation of polyamides from aminoacids (the initial monomer is RAB and there are reactions only between A and B) and polyethers from glycols (RA^2 monomer). In heteropolycondensation the initial mixture usually consists of two symmetrical monomers RA^2 and SB^2 with groups A and B of different types, although there is a possibility of more general processes involving the reaction between RA_1A_2 and SB_1B_2, where groups of the same type in each asymmetric monomer have different reactivities. The heteropolycondensation products ~RSRSR~, typical examples of which are the formation of polyamides from diamines and dicarboxylic acids or the synthesis of polyesters from dicarboxylic acid chlorides and glycols, consist of rigorously alternating monomeric units R and S, i.e. the elementary unit of the homopolymers formed is in this case RS. With the exception of heteropolycondensation, all the processes involving more than one monomer are copolycondensation processes. The simplest characteristic instances of linear copolycondensation are bipolycondensation and interbipolycondensation. An example of the former process is a reaction where at least one of the initial monomers (for example, an aminoacid or a hydroxyacid) is capable of undergoing homopolycondensation under the given conditions. In the second process three monomers, for example $S_1A_1^2 + S_2A_2 + IB^2$, are involved simultaneously, the first two of which, called comonomers, do not react with one another but each is capable of undergoing heteropolycondensation with the third component (the intermonomer). The reactivities of two functional groups of any monomer can be in general different. Processes of this type with an arbitrary number of comonomers are called intercopolycondensation. Furthermore, unless a special stipulation is made, heteropolycondensation and intercopolycondensation imply processes with participation of symmetrical monomers.

1. Ideal Homopolycondensation and Heteropolycondensation

The first computational and theoretical studies on linear polycondensation were published as early as the end of the 1930s.[15,16] In his fundamental investigation[15] Flory calculated for the first time by a statistical method, on the basis of his principle, the MWD of the products of homopolycondensation and heteropolycondensation on the assumption that there is no cyclisation reaction. The number-average degree of polymerisation P_N, the weight distribution function $f_W(l)$ for molecules in terms of the degree of polymerisation l (MWD), and the polydispersity coefficient K_p characterising its width, which Flory[15] calculated for homopolycondensation, are given by the expressions

$$P_N = (1-p)^{-1},\ f_W(l) = (1-p)^2 l p^{l-1},\ K_P = 1+p \qquad (1)$$

and are determined by a single parameter p, which is equal to the conversion of the functional groups. The same formulae describe the products of the heteropolycondensation of an equimolar mixture of monomers and the corresponding formulae have been derived also for non-equimolar initial mixtures[15]. In the latter case the the formula $a_i b^l$ (where $i = 1, 2, 3$) describes the MWD for each of three types of molecules, differing in the type of terminal functional groups, and each has its own value of a_i. Distributions of this kind can be called generalised Flory distributions.

Subsequently these relations were frequently rederived in several different ways. Thus, using the principle of detailed balance, Schulz[16] calculated the MWD for the products of equilibrium homopolycondensation and derived a theoretical relation between the molecular weight of the polymer and the equilibrium constant of the reaction. Subsequently, Meggy[17] extended these results to equilibrium heteropolycondensation. At the beginning of the 1940s Flory[18,52] proposed two thermodynamic methods for the derivation of MWD in equilibrium systems. In the calculation of the most probable Flory distribution [Eqn.(1)] various modifications of the statistical method were used, in particular the treatment was based on a random migration process along a straight line[19] and the convolution integral[20]. The kinetic method has also been widely used in calculations of MWD for a polymer. The Flory distribution [Eqn.(1)] was derived by this method for the products of irreversible[21] and reversible[22] polycondensation in a closed system and also for equilibrium polycondensation[23], taking into account the possible removal of the side product from the reaction zone. In the kinetic schemes adopted[21-23] no account was taken of exchange reactions. It was suggested[24] that their occurrence leads to a narrowing of the MWD compared with the Flory law. However, the simplified kinetic calculation of the MWD in a system where an exchange reaction of the type of alcoholysis or acidolysis takes place and there is no

growth or degradation of macromolecules leads to equilibrium in the distribution defined by Eqn. (1).[25] Examination of the general kinetic scheme for reversible homopolycondensation[26] with allowance for all the reactions mentioned above shows that the products of this process can be described by the Flory distribution at all its stages. Although this type of general kinetic calculation has not been made for heteropolycondensation, there is every reason to believe that, for an equimolar mixture of the initial monomers (only then is there a possibility of the formation of high-molecular-weight products), the MWD for a polymer obtained in an arbitrary reversible process is also determined by Eqn. (1), because the latter has been proved rigorously for two opposite limiting cases: irreversible and equilibrium heteropolycondensation.

A number of studies have been devoted to the theoretical investigation of the influence of the chain termination reaction on the statistical characteristics of the polymer[27-30]. The MWD and the corresponding values of P_N and K_p for the products of homopolycondensation and heteropolycondensation were first calculated by Case[27] using a statistical method. Sokolov et al.[28] calculated analytically and numerically on a computer the values of P_N for a polymer corresponding to different kinetic schemes and mechanisms of the deactivation of functional groups. In particular, they examined termination both by impurities and by a side product formed in the course of the process. An infinite chain of kinetic equations for concentrations of different individual products of irreversible homopolycondensation has been formulated[29,30] with allowance for chain termination by an impurity. The authors did not find an exact solution for this system; certain approximate results are quoted, showing that the chain termination reaction can lead in certain cases to an appreciable narrowing of the MWD.

Statistical[27,31] and kinetic[32] calculations have been made on the heteropolycondensation of two monomers, one of which contains groups having different reactivities. It was shown that the MWD of the products of such a process is described by the generalised Flory distribution, which (for the same value of P_N) is wider the greater the difference between the reactivities of groups of the same type.

The problem of the influence of the rate of supply of one of the monomers to the reaction zone on the statistical characteristics of the products of irreversible heteropolycondensation was investigated by a computational method[33]. Using the kinetic method, the authors showed that the MWD of the polymer is described by the Flory law and the value of P_N may be large even when the condition of the equimolarity of the initial compounds is appreciably infringed, provided that the rate of supply of the monomer taken in excess is sufficiently low. A simple formula was derived in this case, which makes it possible to determine the rate constant for the condensation reaction from the measurements of the dependence of P_N on the rate of supply.

Attention has been drawn to the fact[34] that, in calculations on polycondensation kinetics, account must be taken of the decrease in the volume of the system during the process. The error arising when this fact is ignored reaches several tens per cent according to the author[34].

2. Non-Ideal Systems

Since the MWD of a polymer under the conditions of ideal polycondensation should be described by the Flory distribution with a polydispersity coefficient K_p close to two, any deviation from this value is associated with the breakdown of the ideality of the system. Analysis of experimental data quoted, for example, in Howard's review[35] shows that, together with ideal polycondensation systems, there are also systems which are not consistent with this model. Their MWD is described by broader ($K_p > 2$) or (and this is observed more frequently) narrower ($K_p < 2$) distributions than the Flory distribution. We shall consider further polycondensation models in which account was taken of particular deviations of the system from ideality.

The simplest of these is the model based on the first-order "substitution effect", according to which the reactivities of the functional group of the monomers differ from those of the remaining groups for which the validity of the Flory principle is postulated. Statistical[27] and kinetic[36] calculations have shown that the MWD of the products of irreversible heteropolycondensation of two symmetrical monomers, $RA^2 + SB^2$, the first of which has dependent groups and the second independent groups, is described by the generalised Flory law. Its statistical parameters are expressed in terms of the conversion p, the initial fractions of the monomers, and the relative reactivity κ of the first reacting group of the monomer relative to the remaining second group which has not reacted. Systems with $\kappa \geqslant 0.5$ have the same width of the MWD of the polymer ($K_p = 2$) as if they were ideal and systems with an appreciable accelerating substitution effect, where $\kappa < 0.5$, are characterised by an appreciably greater polydispersity ($2 < K_p < 4$). It is of interest that the formulae for the MWD of the polymer in this system do not differ in their forms from those for the MWD of the polycondensation products in the $RA_1A_2 + SB^2$ monomer system with independent but different groups in one of them. Irreversible heteropolycondensation, where both monomers contain dependent functional groups, has been examined within the framework of the first-order "substitution effect" model[37,38]. Sokolov et al.[37] evaluated numerically on a computer the values of P_N for a polymer corresponding to four different kinetic constants describing all the possible chain propagation reactions in the selected model. The calculations showed that the greater the reactivity of the second groups of the monomers compared with the first, the higher the molecular weight of the polymer obtained for the same conversion. When the difference between the reactivities becomes sufficiently large in both monomers, the process acquires features characteristic of polymerisation, because high-molecular-weight products can be formed for a non-stoichiometric ratio of the initial monomers and an incomplete conversion. Polycondensation systems of this type have not so far been observed experimentally. Case[38] obtained by a statistical method the MWD function for a polymer in the most general case of irreversible heteropolycondensation, where both monomers not only have dependent groups but also groups with different initial reactivities. This function constitutes a generalised Flory distribution analogous to that derived for the heteropolycondensation of monomers with independent groups. However, since a kinetic justification of this result is lacking, the problem of its validity still remains open. For an equilibrium process, this result can be rigorously justified[39] on the basis of fundamental thermodynamic principles. A general algorithm for the calculation of the MWD of equilibrium polycondensation products has been devised[39] for a model based on the "substitution effect" of arbitrary order and the number of independent thermodynamic parameters of this model was indicated.

There is now no doubt that the approximation assuming ideality does not hold for many polycondensation systems and substitution effects must be taken into account in the calculation[6]. In particular, this applies to the polycondensation of aromatic monomers, which frequently have dependent functional groups. In order to justify the "substitution effect" model and determine its parameters, the kinetics of the reactions of bifunctional monomers with the corresponding monofunctional compounds are usually studied under conditions close to those in polycondensation.

Such studies on model systems[40-42,43-47] made it possible to estimate quantitatively the relative reactivity κ of the first or second groups of monomers (bisphenols, dicarboxylic acid dichlorides, aromatic diamines) participating in acceptor-catalytic polyesterification and polyamidaton processes. The results of these investigations[40-47] have shown that $\kappa > 1$ for the majority of the monomers investigated and the first group can be several times more reactive than the second. A combined approach[46,48], which makes it possible to determine the suitability of the "neighbour effect" model for the description of specific non-equilibrium heteropolycondensation processes and at the same time to determine its parameters, is extremely interesting. On the basis of correlations obtained for reaction series of monofunctional compounds, a correlation equation has been derived[46,48] and has been used to calculate four kinetic constants in both the first and second groups for each of twenty different aromatic diamine + dicarboxylic acid dichloride pairs of monomers. These constants were then substituted in the four kinetic equations for the functional groups, which were next solved on a computer. Comparison of the solutions with the experimental data for the kinetics of the initial polycondensation stage showed[46,48] that the agreement is satisfactory in all the twenty systems investigated. A convincing experimental demonstration of the suitability of the "substitution effect" model for the description of equilibrium polycondensation was apparently achieved for the first time by Challa[49-51] in relation to the synthesis of poly(ethylene terephthalate).

In the above studies the influence of the solvent and long-range volume effects on the statistical characteristics of the polymer was completely ignored. Several attempts were made to take these effects into account in the theory of equilibrium polycondensation[52-57]. The equilibrium MWD of the polymer has been calculated[52-55] by minimising the free energy of the system. A term describing the interaction of the polymer molecules with the solvent was added to the expression for the energy. The form of this term was determined by the choice of the specific model of such interaction among those available in the theory of polymeric solutions. First it has been shown for concentrated solutions[52-54] that, for the Flory–Huggins lattice model, the MWD of the equilibrium polycondensation products is described by the Flory law. If other lattice models are used, it is possible to obtain other distributions[54]. It is easy to show[106] that the Flory distribution is obtained when the free energy of the macromolecule varies linearly with the degree of its polymerisation if account is taken of the interaction with the solvent. Among the models considered[54], this condition is satisfied by the Flory–Huggins model alone. The equilibrium MWD of the polymer in dilute solutions, where interactions between the segments of the different chains may be neglected, has been calculated[55-57]. In order to determine the free energy of this system, a number of workers[55,56] also used the lattice model. It was found[55] that in a poor solvent the MWD obtained are narrower, while in effective solvents they are broader than the Flory distribution. Furthermore, in a good solvent there exists a critical number-average degree of polymerisation above which the MWD becomes bimodal[56]. A fairly dilute solution has been examined[57] with the aid of special statistical physical methods, but only in systems close to θ-conditions. The author[57] arrived at results directly opposed to those of Berlin et al.[55]; in a poor solvent the equilibrium MWD of the polymer broadens, while in an effective solvent it becomes narrower compared to the Flory distribution. This contradiction shows, in particular, that in a quantitative study of the influence of long-range order and solvent effects on the statistical characteristics of the products of even equilibrium polycondensation processes, there are still many controversial questions and unsolved problems.

This applies particularly to non-equilibrium processes where the thermodynamic approach is inapplicable. In order to devise a quantitative theory, it is necessary to determine the dependence of the kinetic constants for the elementary reactions between the functional groups on their location in the macromolecules and on the degree of polymerisation of the latter and then to evaluate the statistical characteristics of the polymer from the solution of the corresponding kinetic equations.

There have been several theoretical studies[58-65] whose authors attempted to calculate the MWD of the products of irreversible polycondensation, specifying several empirical relations between the elementary reaction constants and the degree of polymerisation in the kinetic approach[58,59] or between the probability parameters and the degree of polymerisation in the statistical approach[60-65]. Thus the arbitrary relations $k_0(ij)^{-\epsilon}$ [58] and $k_0[1 - \epsilon(i + j)]$ [59] were adopted for the interaction constants of molecules with degrees of polymerisation i and j; the MWD was not calculated but only approximate (for $\epsilon \ll 1$) and cumbersome expressions were found for the concentrations of dimers, trimers, and tetramers[58] or the formulae for P_N and K_p.[59] In an attempt to extend to non-ideal systems Flory's statistical approach to the calculation of the MWD of ideal polycondensation products, a number of workers[60-65] began with the assumption that all ways leading to the formation of a macromolecule with a given degree of polymerisation l are equally probable. The "history" of the formation of the macromolecule is then unimportant; by considering the successive addition of the monomers to one of the growing chains, the authors therefore obtained the formula $f_N = p(1)p(2)\ldots p(l-1)[1 - p(l)]$ for the numerical MWD of the polymer. The investigators[60-65] then selected empirically two- and three-parameter relations between the probability of the formation of the bond $p(l)$ and the degree of polymerisation l of the reacting molecule and found relations between different molecular weights of the polymer and the parameters of the functions $p(l)$.

It is noteworthy that the assumption of equal probabilities of all ways leading to the formation of a molecule with a fixed length is rigorously justified for non-ideal systems only under the conditions of equilibrium[39]. For non-equilibrium processes, there is no such justification and one can actually quote systems (for example, the irreversible homopolycondensation of a monomer RH^2 with dependent groups) where this assumption is invalid. Consequently the formal application of Flory's statistical method to the calculation of the MWD of the products of non-equilibrium non-ideal polycondensation can lead to erroneous results. All the foregoing considerations apply equally to a study[60] where the assumption of equal

probabilities was effectively also used in the derivation of MWD for this process.

Unfortunately there are at present no experimental data whereby one could establish even for a single system a quantitative relation between the chain propagation rate constant and the length of the reacting macromolecules over the entire necessary range of variation of these quantities. For oligomeric molecules, this problem has been studied experimentally in detail on model systems by comparing the rates of reaction of a hydroxy-group with carboxy- [66,67] and isocyanate [68,69] groups in homologous series of compounds differing from one another solely by their molecular weight. It has been shown that, in all the systems investigated, the functional groups of the molecules separated by a bridge with a length corresponding to more than 2–3 methylene units may be regarded as independent and their reactivities may be regarded as identical regardless of the size of the oligomers containing these groups. Consequently in the absence of the substitution effect, i.e. when the above bridge is sufficiently long, Flory's principle holds in reactions between oligomeric molecules. On passing to high-molecular-weight reactants, there is a possibility of deviations from this principle associated with the macromolecular nature of the reactants, i.e. with long-range order effects. The study [70] whose authors investigated for model systems the dependence of the rate constant for the formation of aromatic polycarbonates on the length of the reacting molecules and the nature of the solvent is therefore of interest. In the range of molecular weights investigated (from 6000 to 28 000) it was shown that the reactivity of the functional groups k_θ is independent of the chain length in the θ-solvent and depends only slightly on the length in an effective solvent, where it diminishes to a constant value k_{eff}. The values of k_θ and k_{eff} are close to the polycondensation rate constants in the corresponding solvents and differ from one another approximately by an order of magnitude. The authors [70] attribute this difference to the difference between the densities of the macromolecular coils and hence to the accessibility of the functional groups, depending on the thermodynamic affinity of the polymer and the solvent.

3. Macrocyclisation Reactions

Linear polycondensation processes are frequently accompanied by the formation of cyclic molecules of different sizes. This usually occurs as a result of the condensation of different terminal groups in the same linear molecule, which has assumed a cyclic conformation as a result of the random motion of its segments. There is also a possibility of attack by one of the terminal groups on an internal bond in the same molecule (for example, intramolecular alcoholysis). In all cases the rate constant (or equilibrium constant when equilibrium has been attained) for the corresponding unimolecular reaction is determined by the effective local concentration c established by one of the groups participating in the reaction in the immediate vicinity of another as a result of various conformational rearrangements of the macromolecule containing them. An important feature of intramolecular reactions, which constitutes a fundamental difference between them and intermolecular reactions, is therefore the dependence of their kinetics on the conformational structure of the macromolecules, i.e. on the possible set (taking into account their probabilities) of steric conformations of the molecules. Examination of conformational statistics shows that, even in the absence of the substitution effect, the cyclisation reaction rate constants depend on the degree of polymerisation of the molecule, the only parameter characterising the configurational structure of the homopolymer. This leads to different types of MWD of the products of equilibrium and non-equilibrium processes. Different approaches are therefore required for a quantitative description of processes in these two classes.

It is usually assumed that the rate of intramolecular polycondensation reactions is not limited by the conformational rearrangement of molecular units, because the characteristic times of these reactions as a rule greatly exceed the time required for the attainment of conformational equilibrium. The effective concentration c therefore agrees with the concentration of the corresponding cyclic conformers of linear molecules. Hence information about the size distribution of the cyclic compounds formed, which may be obtained by gas–liquid and gel permeation chromatography [71], can yield useful data about the equilibrium conformational structure of linear chains, provided that an appropriate theory is available. Calculations on equilibrium polycondensation taking into account cyclisation reactions are based on the thermodynamic principle of detailed balancing [72,73]. Thus the Law of Mass Action for condensation and cyclisation reactions, which are respectively reactions of the exchange type and reactions between terminal groups,

$$C_l + C_m \overset{2k}{\rightleftarrows} C_{l+m} + Z,\ C_{l+m} \overset{k_l}{\rightleftarrows} \tilde{C}_l + C_m,\ C_l \overset{k_l'}{\rightleftarrows} \tilde{C}_l + Z \qquad (2)$$

makes it possible to determine the equilibrium concentrations of linear (C_l) and cyclic ($\tilde{C}_l$) l-mers and to relate the equilibrium constants of these reactions:

$$C_l = Z\nu^l/k,\ \tilde{C}_l = k_l\nu^l,\ k_l' = kk_l. \qquad (3)$$

where Z is the concentration of the side product and the parameter ν is determined from the constancy of the total number of monomeric units in the system. It follows from Eqns. (3) that the MWD of linear chains is described by the Flory law but including a parameter ν which is in general not identical with the conversion. In order to determine the MWD for cyclic species and the parameter ν, it is necessary to know the dependence of the equilibrium constant of the second reaction (2) on l. In conformity with thermodynamics, it is determined by the free energy of this reaction. For fairly large values of l, whereupon the heat of this reaction, i.e. the strain in the corresponding ring, is small, k_l is determined solely by the statistics of the steric conformations of linear molecules and may serve as a measure of their flexibility.

In a theoretical study of these conformations, it is usually assumed that the process takes place in a θ-solvent, neglecting, in particular, the long-range volume effects (i.e. the excluded volume effect) and either the statistics of a freely jointed chain or the more realistic rotational isomer model [75,76], whose parameters are known for many systems [76], are used [72–74]. Both these models lead to a normal (Guassian) distribution of the distances between the ends of a chain with l units and hence to an asymmetric behaviour of $k_l \propto l^{-2.5}$, provided that l is large. The rotational isomer model makes it possible to calculate the proportionality coefficient in this formula for many real chains, which depends on the rigidity [76]. Calculation of k_l for low values of l, when it is necessary to take into account the correlations between the directions of the terminal bonds of linear chains assuming cyclic conformations [73,77] as well as deviations from the normal approximation, can be carried out within the framework of the rotational isomer model, or with the aid of a matrix technique [77–83], or by simulating the conformations of the

chain on a computer by the Monte Carlo method[84-87]. Thus the theoretical treatment in the above studies makes it possible to calculate the equilibrium constants k_l, taking into account the above assumptions for the models selected in the relevant studies and then to evaluate the MWD for the reaction products by Eqns. (2) and (3). Here the initial parameters are only the structural characteristics of the polymer chains: valence angles, interatomic bond lengths, and internal rotation potentials. They have been measured independently for a whole series of polymers[76], which permits calculations without using adjustable empirical parameters.

We shall now formulate certain results obtained within the framework of the above theory. The MWD for cyclic molecules is wider compared with the Flory distribution. For a fairly high degree of polymerisation of linear chains, the concentration of rings is independent of the dilution of the system and depends on temperature to only a very slight extent. On the other hand, the weight fractions of all the cyclic molecules in equilibrium depend significantly on the polymer concentration in solution. Thus there exists a critical value of the latter, below which the polycondensation products are virtually only cyclic species[72-74].

The above theoretical conclusions and results, including the values of k_l calculated on the basis of the corresponding rotational isomer models, were tested by studying (by chromatographic methods) the MWD for cyclic products in a large number of equilibrium systems: polyethers[88], polyesters[89-93], polyamides[94-96], polymeric alkylsiloxanes[97], and polysiloxanes[73,78-81,98-105]. In all the systems investigated, the calculated and experimental values of the constants k_l are in good agreement, with the exception of instances corresponding to very low values of l. Cyclic oligomeric dimethylsiloxanes have been studied both experimentally and theoretically in greatest detail[73,78-81,98-101,104,105]. It was found that the experimental values of k_l obtained when the process is carried out in bulk[79,80,104], agree satisfactorily with the values calculated on the basis of the rotational isomer model in the region $8 \leqslant l \leqslant 200$ [80,81,104] (for long rings, fractionation was not carried out), and the Gaussian approximation is valid (Fig. 1) for $l \geqslant 20$. On the other hand, for low values of l ($4 \leqslant l \leqslant 7$) the experimental data are appreciably higher than the theoretical results[79-81,104]. There is no temperature dependence in the region $4 \leqslant l \leqslant 40$ (the process was not investigated for large values of l). Very similar values of k_l were obtained also when the process was carried out in a poor solvent in the vicinity of the θ-point (diethylene glycol at 333 K).[104] A different behaviour was observed in effective solvents. Thus in toluene the experimental data are described satisfactorily by the rotational isomer model only in the region $8 \leqslant l \leqslant 40$ (Fig. 1), while in xylene the values of k_l are independent of the solvent concentration only when $11 \leqslant l \leqslant 40$ and increase with increasing dilution in the region $4 \leqslant l \leqslant 10$.[80,101] Measurements of the weight fraction of cyclic species at different polymer concentrations[80] confirmed the existence of the critical dilution, predicted by the theory[72,74], which is independent of temperature and above which the system consists solely of cyclic molecules. However, the critical concentrations of the polymer proved to be somewhat higher than the theoretical value[80]. Unduly high observed values of k_l for low values of l are usually attributed to the strain in small rings[106] or to the neglect of correlations between the directions of the terminal bonds in short linear chains which have assumed cyclic conformations[73,77]. However, it has been shown for cyclic polydimethylsiloxanes[107,108] that, for $l \geqslant 4$, the ring strain is virtually zero. Correct allowance for correlations between the directions of terminal bonds within the framework of the rotational isomer model also failed to yield a result for $4 \leqslant l \leqslant 7$.[105] The possible cause of the discrepancy with experiment can therefore be the inapplicability of the model to the description of the statistics of the conformations of such small rings. The unduly low theoretical critical dilution of the polymer, starting from which the latter consists of cyclic molecules, is in all probability associated with an incorrect allowance for small rings. The differences between the theoretical and experimental values of k_l for high values of l in an effective solvent (Fig. 1) can be accounted for by long-range volume effects[71,104]. Thus allowance for the excluded volume effect by means of simulation on a computer[109-112] or analytically[113-115] leads to the relation $k_l \propto l^{-2.8 \pm 0.1}$ or a similar relation[109], which agrees fairly well with the experimental values $k_l \propto l^{-2.86}$ and $k_l \propto l^{-2.69}$ obtained by Brown and Slusarczuk[99] and Wright[104] respectively.

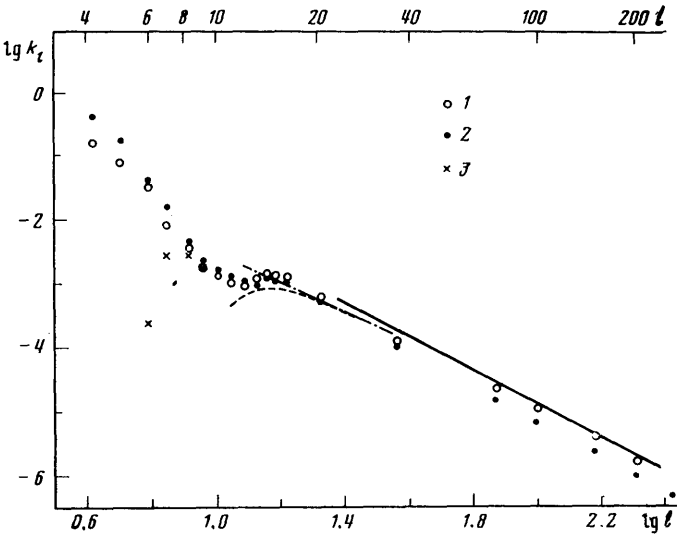


Figure 1. Variation of the equilibrium constants for polydimethylsiloxanes with the degree of polymerisation l. The experimental points were obtained[104] in the absence of a solvent (*1*) and in toluene (*2*) at 383 K. The calculation was performed with the aid of the rotational isomer model in different investigations: continuous line—by Flory and Semlyen[73] (Gaussian approximation); dashed and dot–dash lines—by Suter et al.[105]; 3) by Semlyen and Wright[80].

An important problem is the determination of the relation between the MWD parameters of polymers and their physicochemical properties. An example of this type of study for equilibrium polydimethylsiloxanes is provided by the investigation of Dodgson and Semlyen[116]. Products obtained when the polycondensation was carried out in three different solvents were fractionated to give linear and cyclic components, after which the intrinsic viscosities corresponding to different molecular weights were measured in both fractions. It was found that the relations obtained in a θ-solvent (butanol at 293 K) are very well correlated with the theoretical calculations

predicted previously[117-119]. For example, the ratio of the intrinsic viscosities of the cyclic and linear fractions for identical molecular weights is 0.67, while the theoretical value at the θ-point is 0.662.[116,118,119]

The combined theoretical and experimental studies illustrated above for products of the equilibrium polycondensation of polydimethylsiloxanes make it possible to solve one of the fundamental problems in polymer chemistry: the physicochemical properties of molecules can be determined from their microstructural quantum-mechanical characteristics at least in a θ-solvent. Such studies have been partly carried out also for certain other linear equilibrium polycondensation systems in which cyclisation takes place[71].

The results obtained for irreversible linear polycondensation processes in the presence of intramolecular reactions are much more modest. The MWD for the products of such processes can be calculated only by solving the corresponding kinetic equations, whose form depends on the specific kinetic process mechanism, for example, on whether intramolecular exchange reactions take place or whether cyclisation occurs solely via reactions between terminal functional groups. The rate constant for the reaction between the functional groups of the molecule depends both on its size and on the segmental mobility. As a result of this, even the MWD of linear molecules is not described by the Flory formula in the absence of the substitution effect, which can be readily tested by substituting it in the corresponding kinetic equations.

No general studies have so far been made in order to solve such equations with the aim of investigating the behaviour of the MWD for the products of irreversible polycondensation processes under different conditions, as has been done under equilibrium conditions[72-74]. Solutions of the kinetic equations, derived on the assumption that there are no exchange reactions and no substitution effect, in the interpretation of a specific kinetic experiment[122,123], have been found[120,121]. The kinetics of the formation of lactones from ω-hydroxy acids of the type $HO-(CH_2)l-COOH$ with l between 5 and 24 have been studied[122]. Comparison of the results of this experiment with the solutions of the corresponding kinetic equations made it possible to determine the rate constants for the cyclisation reactions corresponding to different values of l.[120] Sisido[83] showed subsequently that these values are in good agreement with constants which he calculated on the basis of the rotational isomer model for the methylene chain.

The number-average fraction of cyclic polyurethanes, obtained in the reaction of hexamethylene di-isocyanate with poly(ethylene glycols) $HO-(CH_2CH_2O)_{4.5}-OH$ in bulk and in benzene for different dilutions and initial compositions of the monomer mixture, has been measured[123]. By comparing the theoretical expressions with experimental data[123], Gordon and Temple[121] determined the dependence of the cyclisation constants kl on dilution. However, the absence of a rotational isomer model for such chains and the lack of experimental data for the separation of cyclic molecules in terms of their lengths preclude an unambiguous conclusion concerning the applicability of the given theoretical models to the description of the test system.

4. Joint Polycondensation

The molecules of linear copolymers differ, within the limits of the same specimen, by the number of different units (size and composition) and the way in which they alternate in the chain (structure). The equation for the average composition of the products of ideal irreversible interbipolycondensation was obtained independently by Shtraikhman[124] and Beste[125] and the dependence of copolymer composition on conversion for different activities and proportions of the initial monomers was analysed[126] on its basis. If the monomers have dependent functional groups, then in the general case it is not possible to obtain analytical formulae for the composition and the latter must be calculated on a computer[127]. However, it is noteworthy that the problem of calculating the composition of the products of the above process when the initial compounds are supplied simultaneously arises only when their proportions are non-equimolar or when the final reaction products are oligomers. In order to obtain high-molecular-weight products, it is necessary to carry out the reaction between rigorously equimolar amounts of monomers up to nearly 100% conversion. The composition of the copolymer is then always the same as the composition of the initial monomer mixture and the problem of its calculation does not arise.

The first attempt at a quantitative description of the structure of the chains of polycondensation copolymers was undertaken by Beste[125] who calculated the distribution function with respect to length for blocks of various monomeric units in products of ideal intercopolycondensation of a stoichiometric mixture of monomers. For units of the ith type, this function is identical with the Flory distribution having the parameter $b_i = \alpha_i p_i^2$, which depends on the initial fraction of the ith comonomer α_i and the conversion p_i of its groups. It was shown subsequently in relation to interbipolycondensation[128] that this distribution is also obtained in the more general case of an intercomponent with dependent groups, but the parameter b_i is then more complex and is found by numerical calculations on a computer.

A characteristic of the structure of the chains of binary copolymers, which is simple and convenient for theoretical and experimental determination, is the microheterogeneity coefficient K_M, which is expressed in terms of the fractions of different diads of RI and SI elementary units (or triads of monomeric units) by means of the relation

$$K_M = \frac{P(RS)}{P(RS) + 2P(RR)} + \frac{P(RS)}{P(RS) + 2P(SS)}. \quad (4)$$

For a mixture of two homopolymers, $P(RS) = 0$ and correspondingly $K_M = 0$, while for a regularly alternating copolymer $P(RR) = P(SS) = 0$, to which corresponds $K_M = 2$. Between these two extreme cases, corresponding to an ideally ordered arrangement of units in macromolecules, lie all possible values of K_M, $K_M = 1$ corresponding to the fully statistical (i.e. the most disordered) distribution of units. Consequently the degree of order in the copolymer microstructure may be deduced quantitatively from the absolute magnitude of the deviation of K_M from unity, while the tendency of monomeric units towards either a regular alternation in the chains ($K_M > 1$) or (when $K_M < 1$) towards the formation of long blocks of both comonomers can be inferred from the direction of this deviation. The theoretical problem is to express the fraction of the diads in terms of kinetic (for non-equilibrium processes) or thermodynamic (for equilibrium processes) parameters of the system and to find K_M from Eqn. (4).

The kinetic calculation of K_M, carried out for products of irreversible interbipolycondensation[129], showed that the nature of the chain microstructure is determined mainly by the reciprocal relation between the reactivities of the functional groups in the intercomponent. If they are independent, then, according to the theory, $K_M = 1$ and the

distribution of units for any conversion, comonomer ratio, and the activities of the comonomers is always fully statistical. A general correspondence has been established[129], within the framework of a simplified "substitution effect" model, between the nature of the change in the reactivity of the functional groups in the intercomponent in the course of their reaction with the comonomers and the nature of the distribution of the units in the copolymer. If the activity of the second groups of the intercomponent diminishes when the first groups react, a tendency by the chain units to alternate ($K_M > 1$) should be observed; in the opposite case an increase of the reactivity of the second groups should entail the appearance of a tendency towards the formation of blocks ($K_M < 1$). For the same intercomponent with dependent groups, the degree of order in the copolymer microstructure increases with increasing difference between the reactivities of the comonomers. Certain qualitative conclusions concerning the relation between the microstructure of copolymers, the reactivities of the monomers, and the conditions of non-equilibrium interbipolycondensation were reached by Gritsenko[130-132] on the basis of statistical considerations. However, this approach does not make it possible to follow the dynamics of the changes in the microstructure during the process and to relate K_M to the kinetic parameters of the system.

An attempt at a quantitative description of the chain structure in binary copolymers obtained by equilibrium copolycondensation was undertaken by Sawada[133,134], who expressed the fractions of different diads in terms of the thermodynamic parameters of the RR, RS, and SS bonds. K_M for this process was calculated[135] taking into account the non-equimolarity of the initial mixture of monomers.

The use of high-resolution NMR, which makes it possible to determine with a fairly high accuracy (to within ~5%) the fractions of diads of elementary units in the specimen, gives rise to a considerable scope for the investigation of the composition and structure of polycondensation copolymers. The products of both equilibrium and non-equilibrium copolycondensation have been investigated by this method in many specific systems[136,137]. The method has been particularly successful in the latter case, where its use enabled Korshak and coworkers to discover many general features of non-equilibrium interbipolycondensation in relation to acceptor-catalytic copolyesterification[137]. Comparison of the calculated and experimental values of K_M for this case showed that the quantitative agreement between them for different reactivities of the initial compounds and different process conditions was satisfactory[42].

It is noteworthy that the concept of K_M has significance only for copolymers with two types of elementary units, but even in this case K_M does not in general permit an exhaustive description of the copolymer microstructure, i.e. it does not enable one to find the probability of any given sequence of units in it. For arbitrary copolymers, obtained via a polymerisation mechanism, the general problem of the calculation of the microstructure was solved by Price[138], who showed that the molecules of such copolymers may be regarded as individual manifestations of a Markov chain. The mathematical theory of these chains has been thoroughly developed[139], which makes it possible to express the probabilities of any sequences of units in the copolymer in terms of the parameters of the corresponding Markov chain using standard rules and simple algebraic transformations. Kuchanov's study[140], where it was established that the products of an arbitrary homogeneous joint irreversible ideal polycondensation process are described by Markov's chain whose parameters are related in a known manner to the constants of the elementary reactions and the ratios of the initial monomers, is therefore of general importance for the quantitative theory. An analogous result for equilibrium copolycondensation was obtained by Kuchanov and Brun[135], who showed that allowance for arbitrary order in the theory of "substitution effects" does not infringe the Markov nature of the distribution of units in the copolymer. There is no proof that the products of an arbitrary non-equilibrium process have such a property, although it has been obtained[141] for the copolymers formed in the intercopolycondensation of comonomers having independent groups with an intermonomer whose functional groups are dependent.

The problem of the quantitative description of the inhomogeneity of polycondensation copolymers was first considered by Case[27], who calculated by a statistical procedure the distribution function for the molecules with respect to size and composition (SCD) for products of the ideal bipolycondensation of $S_1A_1B_1 + S_2A_2B_2$ monomers. A complete solution of this problem was obtained by Kuchanov[140,141], who proposed a kinetically justified general algorithm for the analytical calculation of the SCD for an arbitrary irreversible ideal copolycondensation, and who derived, as an example, an expression for such distribution in intercopolycondensation. An analogous algorithm for equilibrium processes was devised by Kuchanov and Brun[135]. The demonstration of an unambiguous correspondence between the configurations of the copolymer molecules and the occurrence of a Markov chain enabled the authors[135,140,141] to obtain simple asymptotic formulae for large values of P_N for SCD and the distribution of polycondensation copolymers with respect to composition. For interbipolycondensation, which was considered by the above workers[135,140,141], the above distributions depend solely on the values of three parameters: P_N, the composition of the initial monomer mixtures, and K_M. Analysis of these relations showed that the distribution with respect to composition becomes narrower with increase of P_N and as the block structure of the copolymer becomes more pronounced with increase of K_M.

The study of Korshak and coworkers[142] devoted to the theoretical and experimental investigation of the homopolymers formed in the course of non-equilibrium heteropolycondensation of monomers with an asymmetric distribution of functional groups has a significant bearing on polycondensation theory. In such polymers there is a possibility of the addition of monomers to the chain in two ways—of the "head to head" and "tail to tail" type, on the one hand, and of the "head to tail" type, on the other, as in the homopolymerisation of asymmetric vinyl monomers. It has been shown[142] that a statistical description of such polymers, taking into account the type of addition of their units, can be achieved on the basis of the formulae of copolycondensation theory.

Proceeding now to the consideration of processes involving the formation of block copolymers, the difference between the mechanisms of their formation in equilibrium and non-equilibrium polycondensation reactions is noteworthy. Thus, in the former case, when the mixture of two homopolymers is heated, exchange reactions begin and lead to a redistribution of the monomeric units in the molecules and the formation of block copolymers[6,7]. A quantitative theory of such a process has been developed by Kotlyar[143], who calculated the distribution of blocks with respect to lengths and the content of residual homopolymers in the system. In non-equilibrium interbipoly-

condensation, even of comonomers with markedly different reactivities, statistical copolymers are formed for the simultaneous introduction of all the initial compounds[42,129]. Block copolymers are obtained in such a process when the intermonomer is introduced gradually and fairly slowly into the reaction zone[42,144]. Under these conditions, the average length of the blocks increases to a limit with decrease of the rate of introduction of the intermonomer, the limit being greater the more pronounced the difference between the reactivities of the comonomers. This conclusion and other experimental relations of the parameters of the microstructure of the copolymers and the kinetic constants and methods of introduction of the initial compounds, obtained in non-equilibrium interbipolycondensation, carried out in different ways, are satisfactorily correlated with calculated data[128,136,137].

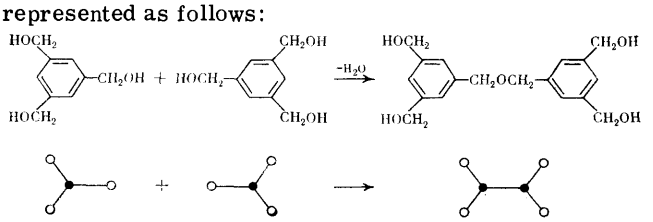
One of the ways of synthesising linear homopolymers and copolymers, widely used in industry, consists of the following steps. An intermediate product is obtained initially in the form of reactive oligomers having terminal functional groups, which are then cross-linked by the polycondensation procedure. The main task of the theory is in this case the determination of quantitative relations between the statistical characteristics of the oligomers, on the one hand, and the polymers formed from them, on the other. In fact, the calculation on such a system is analogous to the calculation on ideal polycondensation. However, in contrast to the latter, the initial compounds can contain different numbers of monomeric units. This problem was considered for the first time by Case[145,146], who calculated by a statistical method the distributions of macromolecules with respect to the degree of polymerisation and the number of oligomeric chains incorporated in them. Bearing in mind that the intermediate oligomers can be obtained both by polycondensation and by ionic and radical polymerisation, Case specified appropriately the MWD for these oligomers. The calculated MWD for the polymer usually differs little from the Flory distribution (1). Only when the cross-linking agent contains functional groups with markedly different reactivities can the MWD for the polymer be significantly narrower[145]. In subsequent studies[21,147,148] an analogous problem was solved for different systems by the kinetic method.

It is noteworthy that molecules with different numbers of useful functional groups (i.e. capable of involvement in further polycondensation) can be formed in the synthesis of the intermediate oligomers. Consequently the concept of "functionality" for such an intermediate has a statistical significance and its quantitative description requires the introduction of a distribution function with respect to the types of functionality (DTF), which determines the number-average and weight-average functionalities of the oligomers[149]. The review of Entelis et al.[149] discusses in detail the possible methods for the determination of DTF for specific oligomers. Systematic experimental studies, permitting a quantitative test of the computational relations established in the studies quoted above, are apparently lacking. We can only note a recent investigation[150], where the influence of the DTF of the initial oligomers on the MWD of the polyurethanes obtained as a result of the cross-linking by di-isocyanates of oligomeric isoprene–butadiene block copolymers with terminal OH groups is the only one that can be mentioned.

III. BRANCHED POLYCONDENSATION

In contrast to linear macromolecules, branched macromolecules can have different steric configurational structures. In order to distinguish individual products of branched polycondensation, it is convenient to represent them schematically by molecular graphs.

(In mathematics a graph is defined[151] as a set of vertices joined by edges.) Each molecule is associated in a one-to-one correspondence with a graph whose topological structure corresponds to the configuration of the given molecule. For example, molecular "trees", i.e. graphs without cyclic fragments, correspond to the products of ideal polycondensation. Chemical bonds are usually associated with the edges of the graph and monomeric units and functional groups are associated with its vertices. Thus the formation of a dimer from two monomeric molecules of a trihydric aromatic alcohol can be represented as follows:



The vertices corresponding to the monomeric units are called nodes (filled circles) and those corresponding to functional groups are referred to as pendant vertices (open circles). Any two nodes of a molecular graph can be connected by a broken line (trail) consisting of edges whose number defines the length of the trail. A linear molecular fragment connecting two monomeric units, called a chain, corresponds to this trail. In the case of trees any pair of nodes is joined by one trail. A definite graph with l nodes corresponds to an arbitrary homopolymer molecule with a degree of polymerisation l (an l-mer) and the number of edges originating from each node of the graph is equal to the functionality of the initial monomer. If several monomers are involved in the process, then the vertices of the graphs corresponding to them are distinguished by colouring the vertices in different ways so that coloured graphs are used for the description of copolymers. The problem of a detailed statistical calculation of the configurational structure of the polymer involves the calculation of the probabilities of various molecular graphs.

An important characteristic of branched polycondensation is gel formation, i.e. the appearance in the system of enormous infusible and insoluble macromolecules having a three-dimensional steric structure‡. Here one can speak of a macrogel or a microgel depending on whether the dimensions of these structures are comparable to those of the reaction apparatus. In the former case, the three-dimensional polymer network occupies the entire reaction volume, while in the latter particles of the microgel are dispersed in it.

Depending on many physicochemical factors (the chemical nature of the polymer formed, its affinity for the solvent, the rate of the cyclisation reaction, etc.) different ways of forming the microgel in branched polycondensation are possible[152]. The simplest involves "homogeneous" gel formation in which the reaction system remains homogeneous during the process up to a certain instant, referred to as the gel point, where it loses fluidity and solubility

‡Only gels formed as a result of a network of covalent bonds and belonging to the first type in Papkov's specification[154] are considered in the present review. Gels of the second or mixed type are disregarded, because of the lack of a quantitative theory of gel formation applicable to them.

almost instantaneously owing to the formation of the macrogel. Together with systems of this kind (we shall henceforth refer to them as classical), there are also others in which the macrogel formation is preceded by the microgel formation stage [153]. In the course of the latter microlayer formation occurs in the system accompanied by the formation of colloid particles whose number and dimensions may vary with time. As a result of the subsequent cross-linking of the microgel particles, they are combined into a single macrogel network. This gel formation mechanism was proposed by Bobalek et al. [153] to account for data concerning the hardening of alkyd resins and was then convincingly demonstrated experimentally in relation to the formation of cross-linked polyurethanes. All attempts at establishing a quantitative theory of gel formation refer solely to classical systems, and an analogous theory for branched polycondensation accompanied by microgel formation is not available.

1. Ideal Systems

In calculations on ideal branched polycondensation various modifications of the statistical approach were used. Together with direct combinatorial considerations use was made of computational methods taken from statistical physics as well as the modern mathematical theory of the enumeration of graphs and of random branching processes. Initially we shall consider in detail studies where calculations were made by these methods of the statistical characteristics of polymers obtained before the onset of gel formation. Next we shall discuss the existing approaches to the description of the process beyond the gel point, and finally we shall illustrate the possibilities of the quantitative theory of branched polycondensation in relation to a specific ideal polycondensation system, investigated in detail by a number of workers both theoretically and experimentally.

Flory [156] was the first to employ a statistical approach to ideal branched systems, having calculated for this purpose all the necessary probabilities (including the probability of an infinitely large molecule, the instant of the appearance of which indicates the onset of gel formation) by means of direct combinatorial procedures. He showed theoretically that gel formation does indeed have pronounced "explosive" properties and is accompanied by an infinite growth of the weight-average molecular weight of the polymer. The conversion of the functional groups p^* at the gel point (the critical conversion) is then independent of temperature, catalyst, dilution, and other process conditions and is determined solely by the functionality of the initial monomers and their fractions. Flory himself considered theoretically only a few specific polycondensation systems [11,156-159] in which not more than one polyfunctional monomer was present, but the computational method which he proposed was later applied to systems which were more complex mathematically. Thus the polycondensation of a polyfunctional monomer with different functional groups, which all react with only one group, has been considered [160,161]. Apart from the MWD, also the distribution function for molecules with respect to different bonds has been calculated. The critical conversion in polycondensation involving several polyfunctional monomers, between which only one elementary reaction takes place, has been calculated in a number of studies [162-167]. In some investigations [165,166] account was taken also of monofunctional additives. Some workers [168-173] calculated the gel point in the polycondensation of various mixtures of mono-, bi-, and poly-functional monomers.

Thus one of the variants of the statistical method, proposed by Flory, has been used until recently in ideal polycondensation systems. However, the corresponding procedure for the calculation of probabilities requires in each specific instance fairly cumbersome and non-evident steps, which was in all probability the reason for the errors made by some investigators using this approach. Thus an incorrect formula has been obtained [162] for the critical conversion in the polycondensation of a polyfunctional monomer with two types of functional groups. Other workers [165,166] incorrectly took into account the influence of monofunctional impurities on the degree of reaction at the gel point [167], while others [172] were unable to attribute the correct statistical significance to the integrals obtained by solving kinetic equations. Finally an attempt has actually been made [174] to construct a statistical scheme for the process, different from that of Flory, on the basis of the same initial postulates, which led to a revision of Flory's fundamental results, including his relation between the critical conversion and the functionality of the initial monomers. However, it was later shown [175-179] that this new scheme is erroneous.

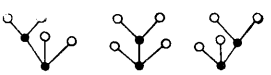
Another variant of the statistical approach to the calculation of the gel point and the MWD (SCD) for the products in ideal polycondensation systems, similar to methods in statistical physics, was proposed by Stockmayer [180-182], who used the fact that, for a fixed conversion, the total number of ways Ω in which all the N monomeric units may be shared between molecules for a given distribution of the latter with respect to the degree of polymerisation in an ideal system is a measure of the probability of the occurrence of such a distribution. For the most probable distribution, Ω has a maximum and in systems with a macroscopic value of N this distribution determines the MWD for the polymer. In order to calculate Ω, it is necessary to solve the problem of the enumeration of all equally probable ways in which the molecular tree with the given number of nodes can be formed. Stockmayer solved this problem by a direct combinatorial calculation for the products of the ideal polycondensation of an arbitrary number of monomers, but only in the case where each monomer has identical groups and only one elementary reaction takes place in the system [181,182].

The application of Stockmayer's statistical method to ideal equilibrium polycondensation has been justified rigorously in a study [183], where Mayer's diagram method [184], well known from the theory of dense gases, was used in succession. As a result it was possible to relate the MWD of the polymer directly to the intramolecular and intermolecular interaction potentials and to calculate various thermodynamic system parameters. The equation of state obtained by Cohen et al. [183] made it possible to draw an analogy between the gel formation phenomenon in polycondensation and the gas–liquid phase transition in the condensation of vapours. Furthermore, the above study threw light on the physical significance of Flory's initial principle and is therefore particularly valuable.

The direct combinatorial method proposed by Stockmayer for the solution of the enumeration problem as well as the corresponding computational scheme proposed by Flory [11,156] are nowadays considered obsolete. It is much more convenient to use for this purpose the methods of graph theory [175,185-195] or the theory of branching processes [196-201], which permit fairly simple and

general calculations on any ideal branched system. Thus the number of different ways in which a molecular tree with a specified number of nodes can be formed is unambiguously related to the symmetry of its configuration, investigated in the theory of graphs [186,187]. The combinatorial entropy of the graph, introduced for the first time by Gordon and Temple [187], can serve as a quantitative measure of this property of the graph. It is noteworthy that Gordon and coworkers [175,186-189] have developed systematically theoretical graph concepts for the description of the products of polycondensation and certain other processes—the so called chemical combinatorial procedure. On the basis of the principle of detailed balancing, they established, for example, a relation between the equilibrium constants of the chemical reactions of branched macromolecules and the combinatorial entropy of the corresponding molecular graphs in ideal polycondensation.

In order to calculate the combinatorial entropy, it is convenient to replace molecular trees by rooted trees. A rooted tree is understood to be one where one of the nodes is distinguished and called the root of the tree [151]. A number equal to the length of the trail connecting any other node with the root is assigned to the given node. This number is called the number of the generation in which the given node is located. A rooted tree is usually represented by a genealogical tree in which all the nodes of a single generation are distributed on a single horizontal line together with all the pendant vertices connected directly to the nodes of the preceding generation. All the possible rooted trees with two trifunctional nodes are represented below:



Evidently two rooted trees can be regarded as identical only if the number and sequence of their vertices (including pendant vertices) in each generation are the same. Having chosen as the root a particular node of the molecular tree and having arranged its vertices in different ways in each generation, we obtain several different rooted trees with the topological structure of the initial molecular tree. It is found [186] that the combinatorial entropy of the latter is related by a simple formula to the number of different rooted trees obtained from it. This number is defined in a standard way in the theory of the enumeration of graphs.

However, the simplest and most universal method of enumerating rooted (genealogical) trees is provided by the theory of random branching processes or more precisely by the Galton-Watson model for such processes [196,197], developed by Good and Otter [198-201]. The formalism corresponding to this theory permits not only a unique enumeration of all such trees but also allows one to determine the probability of each of them. A branching process is one involving the random generation and destruction of particles arranged in the generations of the genealogical tree starting from its root K (Fig. 2) and each particle can reproduce, independently of others, a particular number of new particles (descendants) in the next generation with a specified probability. In the description of branched polycondensation processes either the nodes or the edges between them can be arbitrarily chosen as the particles. The rooted tree represented in Fig. 2 corresponds to one of the individual products of the polycondensation of a trifunctional monomer, the nodes of the tree having been chosen as the particles. The root particle reproduces all others in the first generation; the left-hand particle gives rise in its turn to two particles, while the right-hand particle gives rise to none at all, etc. In the ideal joint polycondensation of several monomers the corresponding molecular and rooted trees contain nodes of different types (a specific colour is assigned to each monomer). The branching process describing such systems must therefore also involve several types of particles, each with its own probabilities of giving rise to a particular number of descendants.

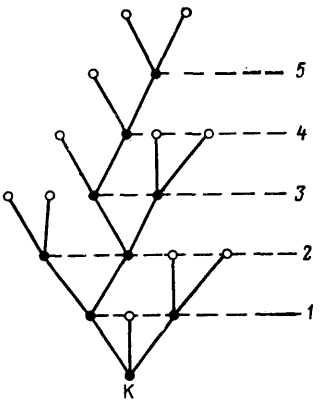


Figure 2. Genealogical tree which is one of the manifestations of a branching process for the ideal polycondensation of a monomer RA^3. The dashed lines connect all the particles of a single generation, whose number is designated by a numeral; K—the root of the tree.

Gordon [202] was the first to suggest that the method of the theory of branching processes be used in calculations on products of ideal branched polycondensation, which led to significant progress in the quantitative description of such systems. Thus the use of a branching process with several types of particles made it possible to calculate [203] fairly simply and uniquely the critical conversions and SCD of a polymer for most general ideal polycondensation systems. Analogous results were obtained independently in some instances by other workers [204,205], who also used for this purpose the theory of branching processes. A rigorous mathematical proof of the applicability of this theory to equilibrium ideal polycondensation processes has been given by Gordon et al. [188]

Another possible approach, which makes it possible to calculate the statistical characteristics of the polymer, consists in the derivation and solution of kinetic equations for the concentrations of various components in a polycondensation process [140,206,207]. When such equations are derived for ideal systems, it is sufficient to distinguish macromolecules solely in terms of the number of functional groups and intramolecular bonds of different types, which significantly facilitates their solution. The results obtained by Kuchanov [140] describe the general irreversible ideal polycondensation process involving an arbitrary number of monomers with any number of types of functional group in each. The SCD of the polymer, found from the solution of the corresponding kinetic equations, agrees

with that calculated with the aid of the theory of branching processes. This confirms that any statistical characteristics of the products of ideal polycondensation processes with specified concentrations of the end groups and intramolecular bonds of all types are independent of whether or not the process takes place under equilibrium conditions. Thus, the critical conversion, MWD, and SCD of the products of ideal branched polycondensation can be calculated in the most general form by both statistical and kinetic methods.

A convenient procedure for the experimental test of the ideality of specific polycondensation systems involves the measurement of the degree of reaction at the gel point, which can be usually done fairly accurately on the basis of the sharp increase of the viscosity of the reaction mixture. The critical conversion has been determined by this method for a fairly large number of systems. When the polycondensation of many of these was carried out in bulk, the experimental values proved to be fairly close to the calculated results obtained by the methods described above. Some of these systems are presented in the Table. The slight discrepancy between theory and experiment can be explained[156] by the occurrence of intramolecular reactions leading to some increase of the critical conversion.

Comparison of the theoretical and experimental conversions at the gel point for certain systems.

System	Monomers			Molar proportions of monomers	p^*_{theor}	p^*_{exp}	Refs.
1	Tricarballylic acid	Adipic acid	Diethylene glycol	0.195:0.707:1	0.88	0.91	156
2	Ditto	Succinic acid	Ditto	0.129:0.806:1	0.92	0.94	156
3	"	Ditto	"	0.270:0.597:1	0.84	0.89	156
4	Benzene-1,3,5-triacetic acid	———	———	———	0.50	0.52	220
5	———	———	1,3,5-Tris-(hydroxymethyl) benzene	———	0.50	0.51	220
6	Benzene-1,3,5-triacetic acid	———	Decamethylene glycol	0.667:1	0.71	0.72	220
7	Tridecanoic acid	———	Pentaerythritol	1.333:1	0.577	0.55	220
8	Lauric acid	Adipic acid	Tris(hydroxymethyl)ethane	1.000:1.000:1	0.866	0.908	166
9	Ditto	Isophthalic acid	Pentaerythritol	1.250:1.375:1	0.696	0.760	166

The statistical characteristics of the products of polycondensation processes examined above do not by themselves yield complete information about the properties of the polymer obtained. Thus many physicochemical parameters of branched macromolecules in solution (average size, intrinsic viscosity, intensity of light scattering, and hydrodynamic Stokes radius) are determined by their conformational and configurational structures. The problem therefore arises of the calculation of the corresponding statistical characteristics of macromolecules by averaging with respect to all their conformations and configurations. In the solution of this problem it is usually assumed[203,208-212] that each chain in the branched macromolecule is freely jointed and is at the same time capable of assuming different conformations regardless of the positions of other parts of the macromolecule. In addition it is postulated that chemical reactions do not affect the conformational equilibrium. These assumptions permit averaging with respect to all the conformations of the molecule with an arbitrary configurational structure and the problem reduces to the calculation of the probabilities of different configurations. In ideal systems methods of the theory of branching processes are again the most suitable for this process. The average dimensions of branched macromolecules formed in the ideal polycondensation of a monomer RA^f [208] and in the polycondensation of several monomers[203] were calculated for the first time with their aid. The theory of branching processes has been applied most logically and fully to the study of the configurational statistics of polycondensation polymers[209-212]. As a result, all the physicochemical parameters enumerated above were calculated by a single method for any ideal branched polycondensation processes, including multicomponent processes[212]. This greatly extends the scope of the experimental test of the theory of such systems. However, one should note the complete neglect in the above calculations of the excluded volume effect, which may play an even greater role in branched polymers than in linear polymers.

So far our discussion of ideal systems was restricted to the purely homogeneous stage of the polycondensation process, up to the gel point. It is important to determine the properties of a classical polycondensation system after the onset of gel formation during the period of the so called hardening when the reaction mixture contains two fractions: the insoluble gel and the dissolved low-molecular-weight sol, the proportion of which decreases with increase of conversion. If the initial postulates of the theory of ideal systems are formally adopted, it is necessary to "prohibit" all intramolecular reactions, including those in the macroscopic gel molecule. The corresponding model was proposed first by Stockmayer[180] and was later developed in detail by Whittle[213]. Here the complete conversion of functional groups cannot exceed a limiting value (equal to $2/f$ for the polycondensation of a monomer RA^f) and the MWD of the sol fraction as well as its average degree of polymerisation remain constant throughout the "hardening" process[213,214] (Fig. 3*a*). The hypotheses underlying this model correspond to virtually infinite rigidity of the gel molecule, as a result of which the effective local concentrations of its end groups in the vicinity of each of them, which determine the rate of the intramolecular reaction, may remain much smaller than their average concentration in the reaction mixture. It is noteworthy that classical systems obeying such rules are not known at the present time[214].

A more realistic model for the calculation of the statistical characteristics of the polymer beyond the gel point was proposed by Flory[156,215]. Here intramolecular reactions are prohibited only in molecules of the sol fraction and Flory's principle of equal activity is assumed to be valid for all the remaining polycondensation reactions, including the cyclisation reactions in the gel. Hence it is assumed that the intramolecular reactions between the functional groups of the gel fraction proceed, like the intermolecular reactions, in conformity with the Law of Mass Action. With these assumptions, all the statistical characteristics of the sol fraction, including the proportion by weight, as for ideal systems up to the onset of gel formation, and the average degree of polymerisation of the molecules beyond the gel point[217] can be calculated by methods of the theory of branching processes for both polycondensation[205,208,216] and copolycondensation systems[203,212]. The results of some of these calculations

for the polycondensation of a trifunctional monomer are presented in Fig. 3*b*. It is noteworthy that the hypothesis of the validity of the Law of Mass Action for reactions between functional groups belonging to the same macroscopic network is not entirely correct even for infinite flexibility of its chains, because here too the motion of its functional groups is not absolutely free and hence absolutely random. Nevertheless, this model gives a much better description than the previous one of the products of real polycondensation processes, which is confirmed by the experimental values of the statistical and physicochemical characteristics of the sol fraction[212,218].

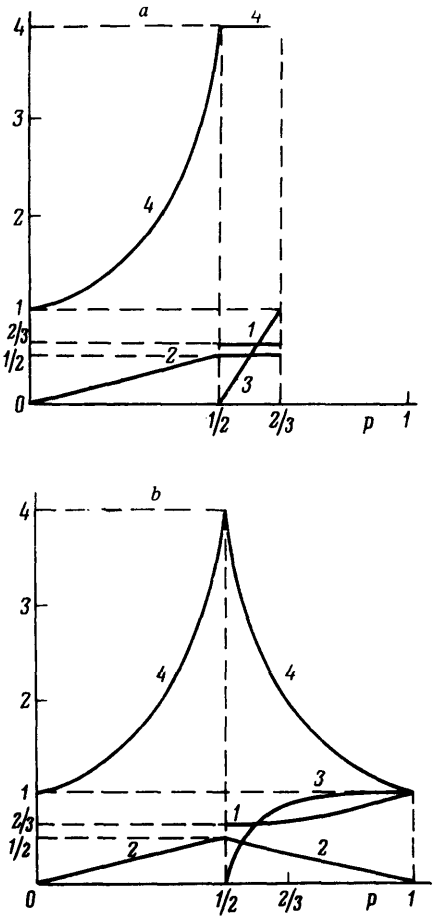


Figure 3. Calculated relations between certain statistical characteristics of the polymer and the conversion of the functional groups in the ideal polycondensation of a monomer RA^3 for the Stockmayer[180] (*a*) and Flory[156] (*b*) models: 1) conversion of the functional groups of the gel fraction; 2) ditto for the sol fraction; 3) proportion by weight of the gel fraction; 4) number-average degree of polymerisation of the sol fraction.

Various theories of the viscoelasticity and swelling of polymer gels[219-221] include as a parameter the number N_e of elastically active chains (EAC)§ of the network. For example, the modulus of elasticity and hence the strain on extension are proportional to N_e.[220] The theory of branching processes makes it possible to calculate N_e and the average length L_e of the EAC in gels formed in ideal polycondensation for the second of the two models discussed above[225]. However, the results obtained can apparently be used only during the initial period of gel formation even in ideal systems. This is because this type of treatment, based on the theory of branching processes, suffers from internal contradictions. On the one hand, a branching process can only be represented by trees, which applies entirely also to the configurational structure of the macroscopic gel molecule. On the other hand, intramolecular reactions in the gel, which are bound to occur beyond the gel point in the model employed, lead to the formation of cyclic fragments. This contradiction entails the so called paradox of "Malthus packing"[214,226,227], consisting in the fact that rooted trees, which are manifestations of the branching process, cannot be accommodated ("packed") in the three-dimensional space beyond the gel point in such a way that the average density of their nodes does not increase without limit as the generation number increases. This follows from the fact that, when $p > p^*$, the average number of particles in each generation, calculated with the aid of the branching process, increases exponentially as $(p/p^*)^n$ with the number n of the generation, whereas the volume in which they must be distributed is proportional to n^3. Only in the immediate vicinity of the gel point ($p/p^* \simeq 1$), where the number of rings in the gel is still relatively small, can one expect the theory to be adequate. Some studies[220,228-230] have demonstrated a satisfactory agreement between the theory and experiment in weakly structured polycondensation gels (Figs. 4 and 5).

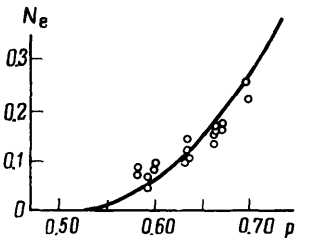


Figure 4. Dependence of the EAC concentration on the conversion determined experimentally from the equilibrium swelling of a phenol-formaldehyde resin[229]. Continuous line—theoretical curve calculated for the corresponding ideal system[220,229].

§This is the name given to any chain bounded by two nodes, each of which has at least three bonds directed to the boundary of the network and containing no other nodes of this kind within it[222-224].

It is noteworthy that the polycondensation reaction in a strongly cross-linked gel cannot proceed under kinetic conditions at all owing to the considerable diffusion-dependent hindrance to the motion of functional groups, which makes it still more difficult to construct an appropriate theory.

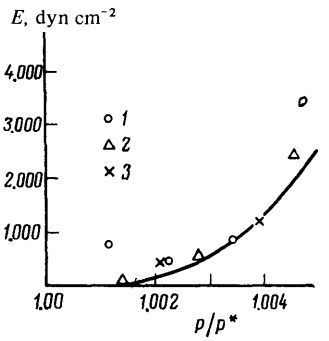


Figure 5. Dependence of the modulus of elasticity E on the conversion of the functional groups for the products of the joint polycondensation of a stoichiometric mixture of decamethylene glycol and benzene-1,3,5-triacetic acid in the melt at 423 K, obtained in three independent experiments (*1–3*) in the "critically branched region" [230]. Continuous line—theoretical curve calculated [230] with the aid of the classical theory of viscoelasticity in which the EAC concentration is evaluated from the formulae for the corresponding ideal system.

Summarising, we may thus say that the theory of ideal branched polycondensation processes is virtually complete only in the field of pre-critical conversions and permits the calculation of the statistical parameters of the reaction products in the immediate vicinity of the gel point. On the other hand, theoretical study of the polymer for higher conversions, particularly of the structure of highly cross-linked gels, constitutes a problem which is still far from being solved. Its solution within the framework of the model of ideal polycondensation is in principle impossible.

The above theoretical results permit the calculation from the known kinetic or thermodynamic parameters of a specific polycondensation system of various statistical characteristics of a polymer obtained for different conversions (both before and after the onset of gel formation) and thus one can obtain extensive information about its structure and about the associated physicochemical and mechanical properties of the products. Combined experimental studies make it possible to establish the adequacy of the ideal model in the process investigated. The initial monomers should then be as far as possible rigid and should have functional groups at a fairly large distance from one another in order to avoid cyclisation and substitution effects. Examples of such monomers have been published [231].

This type of combined study has been recently carried out by Gordon and coworkers [212,218,230,232–236] for the copolycondensation in bulk of a stoichiometric mixture of decamethylene glycol and benzene-1,3,5-triacetic acid. Kinetic measurements established [212] that this reaction is described by a third-order kinetic curve and that its rate is independent of temperature in the range 413–443 K. The weight fractions of both monomers and the dimer, throughout the region up to the gel point, were measured [232] with the aid of gel permeation chromatography and it was possible to compare them with the theoretical values for an ideal system (Fig. 6). The so called critically branched polymer [218], i.e. specimens obtained in the range of conversions directly adjoining the critical conversion both on the left-hand side ($p < p^*$) and on the right-hand side ($p > p^*$), has been studied in particular detail [218]. Thus the value $p^* = 0.720 \pm 0.006$ has been determined with a high accuracy from the measured viscosities of the system in the pre-critical region [230,233] (Fig. 7), which agrees fairly well with the theoretical value $p^* = 1/\sqrt{2} \simeq 0.707$. Hence it was concluded that a "critically branched polymer" contains virtually no rings (not more than one ring bond in one hundred [218]). The modulus of elasticity E was measured by the method developed previously [237] immediately beyond the gel point for different conversions [220,230,233]. Its values also agreed satisfactorily with the calculated results (Fig. 5).

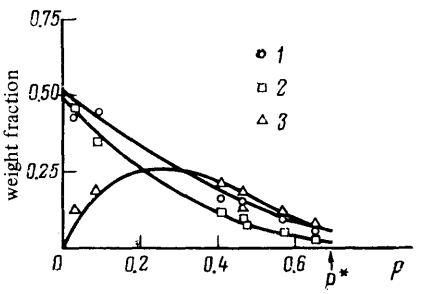


Figure 6. Variation of the weight fractions of decamethylene glycol (*1*), benzene-1,3,5-triacetic acid (*2*), and the corresponding dimer (*3*) with increased conversion of the functional groups in the joint polycondensation of these monomers in the melt at 423 K. The experimental points were obtained [232] by gel permeation chromatography. Continuous lines—theoretical curves for the ideal system [232].

In addition, the following further experiments were performed on the system considered. Specimens of a "critically branched polymer", taken both before the gel point and after it (sol fraction), were stabilised by the addition of monofunctional compounds in order to bind the residual functional groups [234]. The specimens were then dissolved in butanol [236] or ethyl methyl ketone [212,235] at 298 K. The average square of the macromolecular radius z was measured by the light scattering method [212,236] and the sedimentation and diffusion coefficients were determined with the aid of an ultracentrifuge [235] in the solutions thus obtained. The calculation [212,218], carried out with the aid of the theory described above for ideal systems, made it possible to evaluate from these data the weight-average molecular weights of the specimens, which proved to be close to the corresponding values obtained from kinetic and viscometric experiments. In addition, the average distance between the monomeric units in the molecules was calculated. The values of the latter quantity agreed

almost fully for pre-gel and post-gel specimens and were found to be almost independent of the molecular weight[212,218], which also confirms the validity of the theory used in the calculation. Thus extensive experimental and theoretical studies demonstrated the virtually complete adequacy of the ideal polycondensation model for the system under consideration, which gives rise to the hope that the model may be used widely in the investigation of the properties of the products of various branched polycondensation processes.

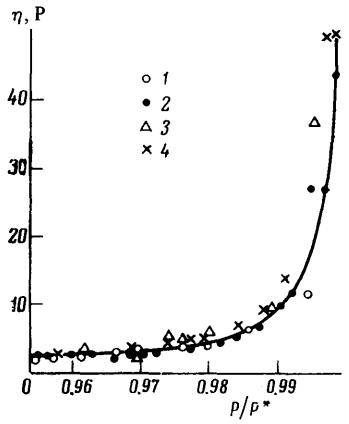


Figure 7. Variation of the viscosity η with the conversion of the functional groups in the "critically branched region" for the same system as in Fig. 5, measured in four independent experiments (*1–4*).[230] The continuous line is described by the theoretical relation between η and the weight-average molecular weight calculated from the formulae for the ideal system [232].

2. The Substitution Effect

As a result of the substitution effect in branched polycondensation, the reactivities of isomers with the same degree of polymerisation may be different. For example, in the first-order substitution effect model, where the activity of an arbitrary functional group depends on the number and positions of groups of each type which have reacted and which are attached to the monomeric unit containing the given group, the reactivity of the molecule is determined by the numbers of its monomeric units with different configurations. It is therefore necessary to distinguish molecules in this model in terms of this feature. Correspondingly, in second-, third-, and higher-order substitution effect models all the molecules are distinguished in terms of the different configurations of pairs, sets of three, etc. adjacent monomeric units present in them. In calculations on the corresponding processes the same methods were used[226,238–246] as for ideal systems but with certain modifications.

The first calculation on a branched polycondensation process taking into account the first-order substitution effect was carried out by Gordon and Scantlebury[238] in the polycondensation of a monomer RA^f. In all the studies published to date, with two exceptions[226,239], the substitution effect was taken into account only within the framework of this model, which will be henceforth assumed to be understood and will no longer be stipulated. Gordon and Scantlebury[238] used the methods of the theory of branching processes in their calculation, but proposed a method for specifying the probabilities of the multiplication of particles different to that in ideal systems. They suggest that the probability that a particle generates a particular number of descendants depends on the configurational structure of the unit corresponding to the particle. Gordon and coworkers believed that their theory describes any polycondensation of a monomer RA^f and they calculate the parameters of the model for two extreme cases: equilibrium and irreversible processes [238]. Gordon and Scantlebury[238] obtained the dependences of the number-average and weight-average molecular weights and of the conversion at the gel point on these parameters, while Dobson and Gordon[208] extended these results to the calculation of the statistical characteristics of the sol fraction of the polymer beyond the gel point. Using a similar computational method, Luby[240] later calculated the distribution of the polymer molecules with respect to the numbers of their monomeric units containing different numbers of groups which have reacted. Gordon and coworkers[238,241] believe that the products of both equilibrium and non-equilibrium polycondensation of any number of arbitrary monomers may be described with the aid of a branching process, taking into account the substitution effect in the monomers, by analogy with ideal systems. In particular, such a process has been indicated[241] for the $RA^2 + SB^f$ system (only groups of different types react) with the substitution effect in both monomers. Since the mathematical apparatus for branching processes makes it possible to calculate all the necessary statistical characteristics of the polymer, Gordon and coworkers thus regard the theory of branched polycondensation with the substitution effect as complete in principle[226].

However, this view is open to objection for several reasons. In the first place the applicability of the methods of the theory of branching processes to calculations on the systems considered was not proved[226,238,241]. The necessity for such proof becomes clear even from an examination of the simplest of these sytems: the polycondensation of a monomer RA^f with allowance for the substitution effect. Analysis showed[239] that the products of the corresponding equilibrium process can indeed be described by methods of this theory. On the other hand, the MWD of the polymer obtained in irreversible polycondensation with the substitution effect does not agree with the formulae of the theory of branching processes. This can be tested by substituting them in the corresponding kinetic equations[12]. Consequently the question of the applicability of the theory of branching processes, like that of any statistical method, to the calculation on each specific polycondensation system with the substitution effect requires separate analysis.

Another statistical approach to the description of the products of equilibrium polycondensation with the substitution effect was proposed by Whittle[242,243]. This method is based on the application of the principle of detailed balancing to specific equilibrium reactions occurring in the system, using in the calculation elements of graph theory. Whittle examined theoretically the polycondensation of both a single monomer RA^f [242] and of several types of monomers $R_iA_i^{f_i}$, but only for the case where the reactions take place between the functional groups of different monomers[243]. His method makes it

possible to calculate the statistical characteristics of the polymer before the onset of gel formation and to calculate the critical conversion at the gel point. For a single monomer, Whittle's results agreed[242] with the corresponding values which follow from the theory of branching processes[238]. For copolycondensation processes, Whittle's study did not reach the stage of computational formulae. Some workers[168,169,244,245] calculated the gel point in specific branched polycondensation processes with the substitution effect by Flory's statistical method having extended it to the case where one of the monomers involved in the process has dependent groups. In these studies[168,169,244] the substitution effect was taken into account only for groups of bifunctional monomers and in that of Durand and Bruneau[245] only for a trifunctional monomer. The study of Kuchanov and Pis'men[246] is the only one where a calculation was performed on the branched polycondensation of monomers with dependent groups by a kinetic method. They proposed a general approach, which makes it possible to derive the corresponding kinetic equations for polycondensation processes in which the substitution effect is significant.

The second-order substitution effect was considered theoretically for the first time by Gordon and Parker[226] for the polycondensation of a monomer RA^f. They suggested that the MWD of the products of the corresponding reactions be described in terms of a branching process. However, as noted above, even in the first-order substitution effect model the statistical characteristics of the products of non-equilibrium polycondensation in such a system cannot be described with the aid of any branching process. This also applies to the second-order substitution effect model. The applicability of the method of the theory of branching processes to the calculation of the products of equilibrium polycondensation within the framework of this model was proved by Brun and Kuchanov[239], who also established a relation between the statistical parameters of the branching process and the thermodynamic parameters of the system. In the formal approach used by Gordon and Parker[226] this relation was not established, which significantly restricted the possibilities for the interpretation of the experiment.

The presence of the substitution effect in branched polycondensation processes was tested in the synthesis of polyesters[241,245,247], polyurethanes[248], and phenol-, melamine-, and urea-formaldehyde resins.[249,250] In particular, a small positive substitution effect, where the bonds formed accelerate the reaction of the terminal groups adjoining the monomeric unit, was established for pentaerythritol, tris(hydroxymethyl)ethane, and tris-(hydroxymethyl)propane in their esterification by adipic or lauric acids[241,247,249]. On the other hand, in the formation of polyurethanes a negative substitution effect was observed[248]. The study of Durand and Bruneau[245] merits most attention among the available experimental investigations. In relation to the polycondensation of tris(hydroxymethyl)propane (SB^3) with adipic (R_1A^2) and lauric (R_2A) acids in the melt, they proposed a general method for testing the adequacy of the substitution model in a specific process and a procedure for determining the parameters of this model. For this purpose, they esterified tris(hydroxymethyl)propane with lauric acid in a preliminary step under the same conditions. The products of this reaction were analysed on a chromatograph and the results were used to determine the fractions of tris-(hydroxymethyl)propane which failed to react and of its mono-, di-, and tri-esters for different conversions. The kinetic constants for the esterification of the functional groups of the same monomers, whose ratios characterise the substitution effect in the triol, were evaluated by comparison with the calculated relations. The conversion at the gel point for the initial process was then calculated from the observed kinetic parameters and was compared with the corresponding value obtained from an independent experiment.

3. Cyclisation in Polycondensation Processes

The intramolecular reactions occurring in the course of branched polycondensation lead to the formation of macromolecules with a particular number of different rings. The corresponding molecular graphs should also contain cyclic fragments. The problem of the identification of such cyclic graphs is much more complex than the corresponding problem for trees. However, its solution is necessary for a complete physically adequate description of intramolecular reactions, because, as already mentioned in the introduction, in contrast to ideal systems the calculation requires allowance for long-range effects in this instance. A rigorous quantitative theory of branched polycondensation accompanied by cyclisation is lacking at the present time, although there have been individual studies[190,206,243,251-261], whose authors attempted to solve the corresponding problem by means of various arbitrary assumptions. However, the latter are more likely to obviate the mathematical difficulties arising in the calculations than to reflect the physical picture of the process. At the same time any scientifically well founded model must take into account to some extent the physicochemical features of the system.

We shall next consider briefly the factors which may influence the course of intramolecular reactions in branched polycondensation and shall point out the possible approaches to their quantitative description. An attempt will also be made to analyse the initial postulates underlying the available models, which permit calculations on the products of the corresponding processes. This is of interest because the authors of the models themselves were not concerned with problems of their physicochemical justification. Although, for the sake of simplicity, we shall discuss only condensation reactions in a homopolymer among all the possible intramolecular transformations, the consideration of analogous reactions in copolymers and also of intramolecular exchange reactions does not alter the qualitative picture of the process.

The elementary step in the intramolecular condensation reaction consists in the interaction of two terminal groups of one molecule with formation of a cyclic fragment in the latter. The probability of such interaction is determined by the relative steric positions of the reacting groups, which depend on the conformational-configurational structure of the molecule. Depending on which pair of functional groups react, particular configurational isomers of the initial molecule will be obtained. Here it is significant that the interaction constants are generally speaking different for each pair. The interconversions of isomers associated with intramolecular reactions therefore have different probabilities. On the other hand, the pair of functional groups which have reacted can be deduced unambiguously from the configurational structures of the initial and final isomers and hence the rate constant for the corresponding unimolecular reaction can be determined (or the corresponding equilibrium constant, if equilibrium is established). Thus, in order to construct

a rigorous theory of branched polycondensation with cyclisation, it is, firstly, necessary to identify in some way all isomers and, secondly, to specify the probabilities of their interconversions. However, the problem can hardly be solved in this general formulation. It is therefore apparently necessary to construct less general models in which the nature of the simplifying assumptions is associated with specific physicochemical characteristics of the system under consideration. These characteristics must determine a particular set of values of constants for the interaction between possible pairs of functional groups in each molecule. By virtue of such model assumptions, there is a possibility of either a significant decrease of the number of transitions between configurational isomers which can occur as a result of intramolecular reactions or many such transitions can become equally probable.

We shall now quote certain considerations concerning the possible selection of these constants. Regardless of whether or not polycondensation is carried out under equilibrium conditions, the probability of the interaction of any two functional groups, say the ith and jth groups, belonging to a macromolecule with a specific configurational structure σ is determined by the effective concentration c_{ij}^{σ} established by one of them in the immediate vicinity of the other for different conformational rearrangements of the molecule in which they are contained. One of the quantities characterising the relative positions of an arbitrary pair of groups in the molecule is the number of chains connecting these groups with one another. In a tree-like molecule, any two functional groups are joined by a single chain. If the fraction of bonds present in cyclic fragments of the molecule (cyclic bonds) is small, a greater proportion of its functional groups possesses this property. It is reasonable to suppose that in this case c_{ij}^{σ} for each pair of such groups depends only on the statistics of the possible conformations of the chain connecting them, which can be determined, as for linear molecules, either by means of the model of a freely jointed chain or the corresponding rotational isomer model. This approximation implies that, in the calculation of the conformational structure, account must be taken only of short-range order effects; the long-range order effects (excluded volume) are neglected. With increase of the number of cyclic bonds, there is an increase of the fraction of functional groups connected by two and more chains. Calculation of the effective concentrations of these groups becomes significantly more complicated. On the one hand, because of the presence of cyclic fragments the corresponding sections of micromolecules contract and become denser, which should lead to an increase of c_{ij}^{σ} and, on the other hand, these sections become more rigid as a result of the appearance of cross-linked structures (skeletons), which prevent the formation of the conformers necessary for the occurrence of the intramolecular reactions. In addition, it is necessary to take into account the possibility of the appearance of loops, nodes, etc.

We shall consider the approaches, described in the literature, to a quantitative description of the products of branched polycondensation accompanied by cyclisation. Here we shall state the conditions which must be imposed on the possible values of c_{ij}^{σ} in a particular model and hence shall define the initial postulates underlying each of them. In the first place we may note that, if we put $c_{ij}^{\sigma} = 0$ for all the functional groups, we arrive at the ideal polycondensation model, naturally subject to the condition that Flory's principle holds for intermolecular interactions, which henceforth will be always understood. In order to carry out calculations on the irreversible polycondensation of a monomer RA^f with allowance for intramolecular reactions, Hoeve[252] extended the statistical Stockmayer method[180]. It was assumed that in the macromolecules formed each monomeric unit may form part of not more than one ring, so that the homopolymer molecules differ not only by the degree of polymerisation, as in Stockmayer's treatment[180], but also by the numbers of monomeric units in rings of different sizes present in them. Hoeve[252] was able to solve the corresponding combinatorial enumeration problem and hence could determine the MWD of the polymer up to the gel point and the critical conversion p^*. His assumption that each monomeric unit belongs to not more than one ring is equivalent to the condition $c_{ij}^{\sigma} = 0$ for all the functional groups connected by two and more chains. It should not influence the result significantly when the number of such groups is comparatively small, i.e. for a small fraction of cyclic bonds. However, the statistical method used in the calculation can be justified only for equilibrium process conditions. On the other hand, the statistical characteristics of the configurational structure of the polymers obtained under the conditions of equilibrium and in its absence should differ in this model (this can be readily shown, for example, for the specific case where $f = 2$). The results obtained[252] for an irreversible process are therefore erroneous. On the other hand, at equilibrium it is possible to deduce from them that the critical conversion p^* is smaller than its value for the corresponding ideal system and to a greater extent the lower of the concentration of monomeric units, i.e. the higher the dilution of the reaction mixture.

In order to deduce the initial postulates underlying other models, we shall consider the effective concentration $c_i^{\sigma} = \sum_j c_{ij}^{\sigma}$ set up in the vicinity of a definite functional group i of a macromolecule by all other groups in this molecule. The quantity c_i^{σ} defines the probability that the ith group is involved in any intramolecular cyclisation reaction and in the general case depends not only on the rigidity and configuration σ of the macromolecule but also on the site occupied by the ith group in the latter.

The same system was considered by Pis'men and Kuchanov[206] as in Hoeve's study[252], but only the kinetic method was used and there were different model assumptions. In the derivation of the corresponding kinetic equations for the concentrations of the macromolecules the authors assumed that the probability of the involvement of a functional group of the molecule in a cyclisation reaction is proportional to the total number of groups in this molecule. Examination of the solution of the equations derived showed[206] that, within the framework of the model considered, the gel point is absent in its classical definition. For a fairly low value of the parameter ϵ (equal to the ratio of the probabilities that the functional groups is involved in intramolecular and intermolecular reactions respectively), the instant of gel formation is defined mathematically not as a point but as a narrow (narrower the lower the value of ϵ) range of conversions, during which there is a sharp change in the weight-average degree of polymerisation, although the latter never becomes infinite[206]. This model corresponds to the assumption that the effective concentration c_{ij}^{σ} for any pair of functional groups in the reaction mixture is the same regardless of, for example, the number and length of the chains

connecting them. Consequently this assumption completely ignores the conformational structure of the molecules. The value of c_i^{σ} for all the functional groups in each macromolecule is then independent of i and is proportional to their total number in the molecule.

On the analogous model assumption, the same system, but under equilibrium conditions, was considered by Harris[251] and Whittle[243] (Harris[251] proposed yet another model, which will be analysed below). In the first of these studies Stockmayer's statistical approach was used[180], but the molecules differed not only by the number l of monomeric units but also by the number s of their intramolecular bonds, so that the probability of any molecule was determined by the values of l and s. It was assumed that any group can form an intramolecular bond without any restrictions, including a cyclic bond, with any group in the system, i.e. no restrictions were imposed on the set of configurations considered. In the second study[243] the calculation was performed with the aid of the principle of detailed balancing together with elements of graph theory. It was found[243] that the weight-average degree of polymerisation of products becomes infinite at an infinitesimal conversion, which is qualitatively inconsistent with the corresponding result[206] for an irreversible process. The absurdity of the value $p^* = 0$ obtained, which the authors themselves noted[243,251], is associated with the complete neglect of the conformational and configurational structure of the molecules in the model. The probability of any molecule with definite values of l and s is in this case proportional to the number of all possible steric configurations with the given values of these quantities. This number increases with increasing l and s (much faster than in the case of trees) and, for macromolecules with a high degree of polymerisation, becomes so large that the probability of a macroscopic gel molecule becomes non-zero however low the conversion.

Another model for calculations on the products of the polycondensation of a monomer RA^f has been proposed by Irzhak et al.[259]. In this case the intramolecular reaction is regarded as one of the variants of chain termination where any functional group can be involved in the cyclisation reaction regardless of the others and can thereby lose the capacity for further participation in the process. In conformity with this hypothesis, it is suggested that the calculation be carried out with the aid of a special branching process. In order to take into account the intramolecular reactions, particles of another type, incapable of multiplication and corresponding to the groups which have reacted with formation of cyclic bonds, were introduced into the model. The model corresponds to the ideal polycondensation of the initial monomer in the presence of a monofunctional impurity giving rise to chain termination, and the model therefore permits a simple calculation of any statistical characteristics of the polymer. Apart from the conversion, a parameter of this model is the probability of cyclisation, i.e. the probability that a group which has reacted is involved in a cyclic bond. The critical conversion p^*, calculated in this way, increases for larger values of this parameter. An attempt has been made[260,261] to calculate it and to justify the proposed model in the case where only groups joined by a single chain can take part in an intramolecular reaction. For this purpose, the probability of the cyclisation of any group is represented by the sum of the probabilities of their reaction with formation of rings of all possible sizes. In the calculation of these probabilities use is made of the conformational statistics of a freely jointed chain and also of the hypothesis that the size of any ring formed when two groups interact is equal to the difference between the numbers of generations of the genealogical tree (Fig. 2) in which they are located. However, such an attempt to calculate the probability parameters within the framework of the same statistical method is incorrect, because two functional groups, even those in the same generation, may be joined by a chain of arbitrary length and therefore the ring formed when they react can also be of any size. In fact the model proposed by the authors[259-261] is based on the hypothesis that the effective concentration c_i^{σ} for any functional group in the reaction system is independent at each instant of the molecule to which the given group belongs and of the site where it is located within the molecule. This is equivalent to the employment of the Flory principle for intramolecular reactions. Hence it follows, in particular, that the statistical characteristics of products, including the critical conversion, are independent, as for ideal polycondensation, of whether or not the process is carried out under equilibrium conditions.

In fact this hypothesis also constituted the basis of an earlier study by Kilb[253], who calculated the critical conversions in the $RA^2 + SB^f$ and $RA^2 + S_1B^2 + S_2B^f$ systems, in which the condensation reaction takes place only between groups of different types. Kilb was able to complete the calculation only for the first of these systems. In contrast to previous workers, he used for this purpose Flory's statistical method, which is fairly cumbersome and is not one most convenient for calculation, having extended it to the case where each functional group can be involved in the cyclisation reaction with a certain probability. Although this computational scheme is technically more complex than that employed in other studies[259-261] (particularly because the assumptions underlying it are less evident), the two schemes are fully equivalent from the standpoint of the final results. All the conclusions and remarks which we have made concerning the initial postulates of the model devised by Irzhak and coworkers[259-261], including the cyclisation probabilities associated with the calculation, are fully applicable also to Kilb's results[253].

Yet another model for calculations on the equilibrium polycondensation of the monomer RA^f accompanied by cyclisation, which resembles, from the standpoint of the initial assumptions, the models just described, was proposed by Harris[251] in order to obtain more likely results than those which follow from his first model. He again used Stockmayer's method, distinguishing molecules in terms of the degree of polymerisation and the number of bonds, but he significantly decreased the number of allowed steric configurations. Harris suggested for this purpose that each functional group of the molecule, having the configurational structure of a tree, can form a cyclic bond with a definite number of other groups of the same molecule, which is independent of the degree of its polymerisation (but not with all the groups, as in the first model). With increase of the number of cyclic bonds in the molecule, the number of groups remaining in it diminishes and there is a proportional decrease of the number of groups capable of forming a bond with the given group. On these assumptions, Harris was able to complete the calculation of only the gel point for the system. It was found that the critical conversion increases with dilution of the reaction mixture and there exists a dilution above which there is no gel formation whatever the conversion. The initial assumptions of Harris's model are as follows. Flory's principle holds for the

intramolecular reactions of the functional groups of tree-like molecules, i.e. the concentration c_i^{σ} for such molecules is independent of both i and σ. For the groups of other molecules, the values of c_i^{σ} depend only on σ and decrease with increase of the number of cyclic bonds in proportion to the number of terminal groups remaining in the molecules.

Finally, we shall consider the computational scheme proposed by Gordon and coworkers [254-258]. It makes it possible to calculate the statistical characteristics of the polycondensation and cyclisation products derived from one and several monomers, both before and after the gel point, including the critical conversion, even in the presence of the substitution effect. For this purpose, the authors [254-258] suggest that a branching process be used with an additional type of particles, corresponding to the functional groups which have reacted with formation of cyclic bonds. However, in contrast to Irzhak and coworkers [259-261], Gordon and coworkers suggest [254] that the probability that an arbitrary particle reproduces a particular number of other particles in the next generation depends, as for the first order substitution effect, on the number of functional groups which have reacted in the monomeric unit corresponding to the given particle. The authors [254-258] believe that the computational scheme which they proposed can describe fairly satisfactorily any branched polycondensation process involving intramolecular reactions regardless of whether or not it is carried out under equilibrium conditions, provided that the probability parameters of the corresponding branching process are specified in the appropriate manner. They also attempted to justify their model for the case where only functional groups linked by a single chain can participate in the cyclisation reaction, so that each edge of the molecular graph can form part of not more than one ring. By cutting any one edge in such a ring in an arbitrary fashion, it is possible to convert the set of such cyclic graphs into the corresponding set of trees. (In the theory of graphs the trees thus obtained are called chord trees, hence the name "the model of chord trees" [257].) Pendant vertices of yet another type, called cyclic, which appear in pairs as a result of each cut, are added in this procedure. It is suggested that [257,258] these trees, represented as rooted trees, are manifestations of the branching process.

However, this interpretation, which does not go beyond the framework of the statistical method itself, is incorrect. Indeed, suppose that two cyclic vertices, separated by a trail of length n, appear on cutting an edge. If one of the vertices is located in a certain generation of the genealogical tree, the other must be present in one of the nearest n generations. However, such obligatory appearance of particles of a specified type cannot be described, in principle, by any branching process whose particles reproduce others independently in each generation. The chord tree model is actually based on the assumption that the value of c_i^{σ} for an arbitrary functional group is determined solely by the number of groups which have already reacted in the monomeric unit containing it and is proportional to this number, i.e. the method is based on one of the variants of the generalised Flory principle for cyclisation reactions.

Thus, despite the fairly large number of models proposed, the problem of the theoretical description of branched polycondensation processes accompanied by intramolecular reactions is virtually in the very initial stage of its solution. In fact all the models now available are based on various arbitrary assumptions in no way related to specific physicochemical features of the systems considered. In particular, Flory's principle for intramolecular reactions, in contrast to intermolecular reactions, still has no physicochemical justification. Because of this, one cannot at present specify even approximately the class of suggested systems described by a particular model among those described above. The only way of testing their adequacy therefore involves a comparison of calculated results with experimental data for specific processes. However, the available experimental data [262-268] do not permit a sufficiently correct solution of the problem for systems investigated in the studies quoted above, since it is not known what contribution arises from intramolecular reactions proper relative to ideal systems. Furthermore, when attempts were made to compare the theory with experiment [263-268], the authors used adjustable parameters whose values were not determined from independent experimental data.

In conclusion we may note that, as shown by recent studies [269-274], the diagram technique of the theory of quantum fields [269] and the simulation of the process on a computer by the Monte Carlo method [270-274] may prove promising in the development of new computational methods for the solution of the problem of taking into account intramolecular reactions in branched polycondensation.

4. Related Systems

The methods for the quantitative description of branched polycondensation analysed above can be applied in the calculation on many other systems. They include the cross-linking of reactive oligomers by the polycondensation method, cyclotrimerisation, certain processes involving the synthesis of inorganic polymers, and others.

The synthesis of a three-dimensional polymer frequently takes place in two stages: oligomeric chains with terminal functional groups are obtained initially and are then structured in the presence of a bifunctional cross-linking agent. If the intermediate oligomers are linear, a polyfunctional branching agent is also added. A quantitative description of the products of such processes requires the solution of two different problems. The first consists in finding the distribution with respect to the lengths of internodal chains and the free ends of the macromolecules, while the second consists in determining the probabilities of various steric configurations of branched polymers.

Virtually all the published theoretical studies [275-278] were devoted to the first, simpler of the two problems. As stated in an early investigation by Case [275], the approach to its solution is analogous to that used in the calculation of the MWD of cross-linked linear polymers. However, in terms of the general formulation, where the initial compounds have arbitrary MWD and functionalities, this type of problem has not been solved. Calculations have only been made on certain specific systems by statistical [275,278] and kinetic [276,277] methods.

The same methods as in calculations on the products of branched polycondensation can be used in the solution of the second problem. In particular, when ideality of the system is assumed, the dependence of the gel point on the functionalities and proportions of the initial compounds may be found from the formulae for the corresponding ideal polycondensation. The justification of this calculation was demonstrated experimentally in relation to structure formation in oligobutadiene di-isocyanates with the

aid of an aromatic triamine.[279] A method has been proposed[280] for the determination of the weight-average functionality of polymers undergoing cross-linking, from the measurement of the gel point during their hardening. It employs computational formulae[181] for the dependence of the critical conversion p^* on the functionality of the initial monomers in ideal polycondensation. This method has been used to determine the functionality of oligobutadienes with terminal carboxy-[281,282] and hydroxy-groups[282] with glycerol[281] and hexamethylene di-isocyanate[282] as the cross-linking agents.

A study by Zabrodin et al.[283] was devoted to the calculation of the statistical characteristics of the branched polymers obtained when oligomers with reactive terminal groups are cross-linked by the polycondensation method. The proportions by weight of the free ends and of the gel fraction as well as the concentrations of its elastically active chains were calculated by the statistical method assuming that the system is ideal.

From the standpoint of the theory, polycyclotrimerisation processes, which constitute a promising method for the synthesis of three-dimensional polymers, are very close to polycondensation[284,285]. Six-membered elementary carbocycles and heterocycles, each of which is formed in the reaction of three functional groups of the monomers, serve as intramolecular linkages in this instance. Since the branching capacity m of an intramolecular linkage in such polymers is three (whereas in polycondensation products it is $m = 2$) gel formation is possible even in the polycyclotrimerisation of bifunctional monomers ($f = 2$). A rigorous quantitative theory of polycyclotrimerisation and of the analogous more general processes with an arbitrary value of m has been developed by Yamabe and Fukui[258-288] on the assumption that the system is ideal. Using Stockmayer's statistical method[180], they calculated the MWD and the gel point of the products of the polycyclotrimerisation of a monomer having an arbitrary functionality f and then extended these results to any value of m and an arbitrary distribution of the initial compounds with respect to the number of their functional groups. The authors[288] then set up a general quantitative theory of reactions involving the simultaneous formation of intramolecular linkages of different functionalities m. In the same study[288] the MWD and the proportion by weight of the sol fraction were calculated. In an attempt to take into account the formation of non-elementary rings in the polymer the authors[286] used in the calculation of the MWD of the cyclotrimerisation product the statistical approach devised by Harris[251], which he used to describe polycondensation processes. Naturally all the critical remarks made above concerning the justification and the limits of applicability of this approach remain in force also for cyclotrimerisation. A calculation on this process without taking into account macrorings can be carried out also with the aid of the methods of the theory of branching processes[289].

The quantitative theory of polycondensation can be applied also to the description of the equilibrium products of processes involving the formation of inorganic polymers. Here it is necessary to establish which structural units in such polymers correspond to the monomeric units, intramolecular linkages, and terminal functional groups in polycondensation macromolecules. Certain ligands usually correspond to monomeric units, while bridging atoms (for example, oxygen or sulphur) or groups of atoms correspond to intramolecular bonds. Thus the theory of ideal branched polycondensation has been applied[290] to silicate melts. The experimental gel point, the weight fraction of the gel beyond the gel point, and the concentrations of mono-, tri-, and tetra-mers were compared with the values calculated from the formulae of this theory. The experimental and theoretical gel points virtually agreed, but no such agreement was obtained for the weight fractions of the gel at some distance from the gel point. According to the author[290], this is associated with the intense cyclisation beyond the gel point.

Numerous experimental studies by Van Wazer and coworkers[291] were devoted to the investigation of various phosphorus-containing polymers, for example, poly-(phosphoryl chloride), polyphosphoryldimethylamide, polyphosphate esters, polyphosphorothioate esters, and others. An appropriate theory, using the methods for the enumeration of graphs, was devised for their quantitative description[292,293]. The results obtained in these studies[292,293] actually correspond to those which arise from the theory of branched equilibrium polycondensation taking into account the substitution effect[238]. This theory makes it possible to calculate the critical conversion at the gel point from the known equilibrium concentrations of the monomeric units with a definite number of linkages. These concentrations for a number of phosphorus-containing polymers have been found experimentally from NMR spectra[294-297]. The conversions at the gel point, evaluated from these experimental data, are in satisfactory agreement with the values determined in the same studies[294-297] by the viscometric method. The results confirm the validity of the "substitution effect" model for the description of the inorganic systems investigated.

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The general quantitative theory of ideal systems, permitting the calculation of the most important physicochemical parameters of the products of many specific polycondensation processes, which may be regarded as ideal with adequate accuracy for practical purposes, can now be regarded as complete. At the same time there are just as many systems which, for different reasons, are not described by this theory. Calculations on such systems require the allowance for various factors in the kinetic model leading to the deviation of the system from ideality. The greatest advances have been achieved in this field in the quantitative description of polycondensation with the substitution effect owing to the possibility of employing the generalised Flory principle. Much more modest results have been obtained in attempts to take into account in the theory the long-range order effects, which are decisive when molecular cyclisation is considered, and also the possible influence of the conformational and configurational structure of the molecules on the reactivity of their functional groups. The number of unsolved problems in this field greatly exceeds the number of those which have been solved, which is due to the necessity to take into account the conformational statistics of macromolecules in kinetic calculations. Progress in the development of the theory of such non-ideal systems is possible only when joint efforts are made by chemists and physicists, since the given problem lies at the boundary between chemical kinetics and the statistical physics of polymers.

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Trimerisation Polycondensation of Aromatic Acetyl Compounds and Their Ketals†

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The methods of synthesis, principal properties, and aspects of the application of polyphenylenes obtained by the trimerisation polycyclocondensation (PCC) of aromatic acetyl compounds or their ketals are examined. Attention is concentrated on the analysis of the influence of the conditions of synthesis on the cyclisation process.
The bibliography includes 51 references.

CONTENTS

I. Introduction 189
II. PCC of aromatic acetyl compounds 189
III. PCC of the ketals of aromatic acetyl compounds 190
IV. Practical applications of polyphenylenes based on aromatic acetyl compounds and their ketals 196

I. INTRODUCTION

One of the promising classes of thermostable polymers comprises polyphenylenes, the high thermal and chemical stability of which make it possible to use them as binders for various reinforced and antifriction materials and for other purposes.

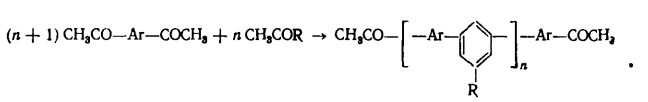
Polyphenylenes are synthesised nowadays in various ways using a wide variety of initial monomers[1,2]. The known methods for the formation of polyphenylenes suffer from various disadvantages. Progress in the field of synthesis and particularly in the application of polyphenylenes will be determined primarily by advances in the synthesis of polymers capable of being easily worked to form various articles, i.e. polymers which are readily soluble in organic solvents, and the methods of their synthesis should be technologically viable and based on available initial monomers.

The present review deals with the synthesis and properties of polyphenylenes obtained by the trimerisation polycyclocondensation (PCC) of acetyl compounds (methyl ketones) or their ketals. On the one hand, trimerisation PCC is genetically related to polycyclotrimerisation processes, which have been considered in detail in a review[3], and on the other, this process is a specific form of PCC, the general characteristics of which have already been examined[4]. In the present review attention is concentrated on factors influencing cyclisation, since, depending on the process conditions, both the degree of completion and specific features of PCC may vary and the contribution of the branching and cross-linking reactions may increase. This can ultimately lead to an increase of the fraction of defective structures which impair the useful properties of polymers (defective sections are as a rule least thermostable and are the first to undergo degradative processes).

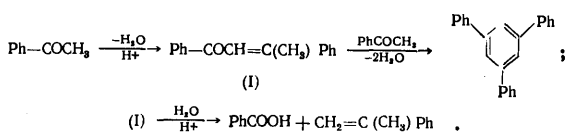
II. PCC OF AROMATIC ACETYL COMPOUNDS

The use of aromatic di- and mono-acetyl compounds as the initial monomers under PCC conditions made it possible to develop a new method for the synthesis of polymers of the polyphenylene type[5]. The method is based on the cyclocondensation of methyl ketones (acetone[6], acetophenone[7], and various aryl methyl or alkylaryl methyl ketones[8,9]) in the presence of acid catalysts, which has been known for a long time in organic chemistry.

Under the conditions of equal reactivities and without allowance for side reactions, polycyclocondensation involving the formation of polyphenylenes can be represented schematically as follows:



The actual process is complicated by side reactions, mainly incomplete cyclisation, and the unequal reactivities of the monomers. The cyclisation of aryl methyl ketones with formation of a benzene ring in an acid medium[8] proceeds via a dimer stage dypnone (β-methylchalcone), but dypnone can react with the liberated water to form an acid and α-methylstyrene[10]:

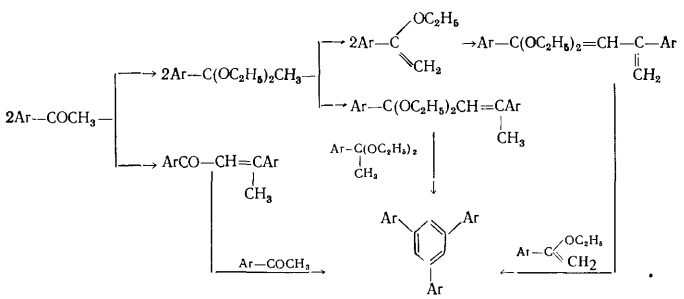


Acids or Lewis acids, which can simultaneously bind the water formed (H_2SO_4, $ZnCl_2$, polyphosphoric acid, BF_3, $BeCl_2$, $AlCl_3$, $AlBr_3$, dry HCl, and others) as well as certain other compounds, are therefore used as PCC catalysts[5]. The specificity of the formation of polyphenylenes under these conditions is open to doubt, since the yield of triphenylbenzenes from acetophenone does not exceed 20–50%.[9]

Korshak and coworkers[11,12] suggested that PCC of aromatic di- and mono-acetyl compounds be carried out in the presence of dry HCl and ethyl orthoformate in an inert solvent at approximately 20°C and put forward a

†Review commemorating the 70th Birthday of Academician V. V. Korshak.

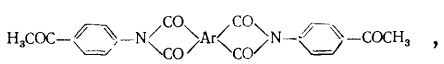
mechanism for the elementary step involving the formation of polyphenylenes under the conditions indicated:



The PCC reaction in solution was stopped at the stage of soluble polyphenylenes with a relatively low molecular weight and residual end groups (fore-polyphenylenes), which were isolated and then converted on heating above 250°C into three-dimensional polymers as a result of further condensation of the end groups. By carrying out the process in two stages, it was possible to convert the polymers into finished articles in the second stage. The monomers used were acetophenone, *p*-diacetylbenzene, di(acetylphenyl) ether, diacetylbiphenyl, and other compounds. Equimolar or nearly equimolar proportions of the initial monomers proved to be optimal[12]. A detailed chemical study of pre-polyphenylenes obtained by the above procedure[13] showed that the chain contained approximately two defective dypnone fragments.

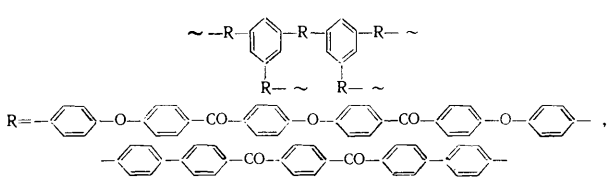
The employment of a single bifunctional monomer (diacetylferrocene) by Schlögl and Soukup[14] in an analogous process led to the formation of a three-dimensional product which could not be worked.

The use of bisacetylimides having the general formula



which made it possible to obtained cross-linked thermostable polymers by thermal polycyclocondensation, proved to be of interest[15]. The authors note that, when the process is carried out at 400°C without a catalyst, the product contains a fairly large number of defective structures, namely dypnone structures.

Zaitsev and coworkers[16,17] obtained cross-linked polymers having the general formula



and investigated their thermal stability.

Polymers based on the diacetyldibenzyl derivatives of *o*-, *m*-, or *p*-carbaboranes, obtained in the presence of HCl and ethyl orthoformate, proved to be the most thermostable[18,19]. The pre-polymers obtained with an average molecular weight of 1100–4600 contained, together with 1,3,5-triphenylbenzene units, also dypnone fragments and acetyl and ketal end groups. They were all readily soluble in many organic solvents: chloroform, toluene, dioxan, acetone, and others. After heat treatment at 400–450°C, they were converted into three-dimensional polymers with high thermal stability and heat resistance (according to the results of thermogravimetric analysis, no weight loss was observed on heating in air up to 900°C).

III. PCC OF THE KETALS OF AROMATIC ACETYL COMPOUNDS

Use of ketals of aromatic acetyl compounds makes it possible to carry out the PCC process more specifically and with formation of less defective structures. Korshak et al.[20] proposed a method for the synthesis of polyphenylenes from the ethyl ketals of aromatic di- and mono-acetyl compounds under conditions analogous to the PCC of aromatic acetyl compounds in the presence of ethyl orthoformate.

1. The Study of the PCC of Ketals in Model Reactions

The optimum conditions for the synthesis of polyphenylenes were discovered in the cyclocondensation of the acetophenone ketal[21,22], which simulates the PCC process. The efficiencies of various acid catalysts were estimated in this model reaction[21]. It was found that gaseous hydrogen chloride, the chlorides of inorganic and organic acids which form HCl on interaction with the alcohol liberated in the synthesis, and toluene-*p*-sulphonic acid are the most efficient catalysts. The high catalytic activity of HCl is associated with the ease of its dissociation in aprotic solvents: $HCl \rightleftharpoons H^+ + HCl_2^-$. It was established[22] that the maximum yield of 1,3,5-triphenylbenzene in the presence of HCl is observed at an initial ketal concentration in solution of approximately 1 M, the relation passing through an extremum. It can be accounted for by the complexity of the cyclocondensation process, i.e. by the occurrence, together with trimerisation PCC, of various condensation and cyclocondensation side reactions.

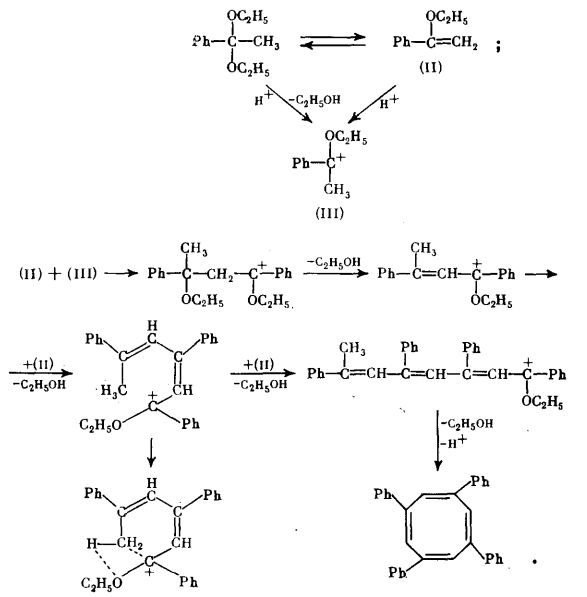
Table 1. The influence of solvent polarity μ on the yield of 1,3,5-triphenylbenzene (catalyst HCl, temperature 20°C, reaction time 1 h).

Solvent	μ	Yield %	Solvent	μ	Yield, %
Benzene	0.00	78	*m*-Cresol	1.54	43
CCl_4	0.00	72	Chlorobenzene	1.56	42
Toluene	0.29	76	Dimethylformamide	3.37	27
Dioxan	0.45	69	Nitrobenzene	3.99	29
$CHCl_3$	1.15	60			

The nature of the cyclocondensation of ketals is significantly influenced by the nature of the solvent (Table 1).[21] It was found that with increase of the polarity of the solvent, the yield of 1,3,5-triphenylbenzene falls. In highly polar solvents, such as nitrobenzene and dimethylformamide, the yield was less than 30%.

The study of the kinetics of the cyclocondensation of the acetophenone ketal under optimum conditions with respect to both the 1,3,5-triphenylbenzene formed[23] and the alcohol liberated in the course of cyclocondensation[21] showed that the process is of second order with respect to the ketal. The rate constants at 20°C, calculated by a second-order kinetic equation for various initial ketal concentrations, were approximately 1.2×10^{-1} litre mole^{-1} min^{-1}.

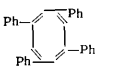
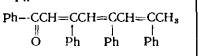
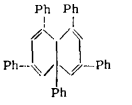
A mechanism for the cyclocondensation of ketals taking into account the kinetic data was proposed[21]. According to this mechanism, the cyclocondensation process proceeds as follows. Equilibrium is established in an acid medium with formation of α-ethoxystyrene from the acetophenone ketals. The addition of a proton to both the acetophenone ketal and to α-ethoxystyrene results in the formation of a carbonium ion. The subsequent interaction involves electrophilic attack by the carbonium ion on the carbon atom of the methylene group in α-ethoxystyrene, which is polarised owing to the presence of an oxygen atom next to the double bond of the vinyl ether group. Intramolecular elimination of the alcohol leads to the formation of a more stable form of the dimer, stabilised as a result of conjugation. Subsequent addition of yet another molecule to α-ethoxystyrene gives a trimer which is either converted into 1,3,5-triphenylbenzene via the formation of an intermediate complex followed by a cyclic electron transfer, or it interacts with a new α-ethoxystyrene molecule to form a tetramer, etc. The process can be represented schematically as follows:



The above scheme is confirmed by many facts, for example, the formation of triphenylbenzene in 68% yield from α-ethoxystyrene in benzene solution on treatment with HCl [21] and in addition by the mass-spectrometric analysis of the products of the cyclocondensation of acetophenone ketal[24]. Table 2 shows that, together with the main product (1,3,5-triphenylbenzene), the mixture contains α-ethoxystyrene, dypnone, 1,3,5,7-tetraphenylcyclo-octatetraene, a linear tetramer, and a cyclic pentamer, which, according to van Tamelen and Burkoth[25], should exist as 9,10-dihydronaphthalene. Analysis of the reaction mixture on a gas chromatograph combined with a mass spectrometer showed that the above compounds give rise to individual peaks corresponding to molecular ions. The presence of ketones is explained by the hydrolysis of the ketals in the course of isolation.

The proposed mechanism explains certain features of the cyclocondensation and polycyclocondensation of ketals. For example, the dependence of the yield of the trimer on the polarity of the medium, indicated above, can be accounted for by the effects of the stabilisation of the carbonium ion and the decrease of its reactivity.

Table 2. Mass-spectrometric analysis of the condensation products of the acetophenone ketal.

m/e	Compound corresponding to the molecular ion	Relative peak intensity, %		
		c_0^*=0.25 M	c_0=1.0 M	c_0=1.5 M
148	α-Ethoxystyrene	8	2.5	11.4
222	Dypnone	17	22	26
306	1,3,5-Triphenylbenzene	66	71	57.5
408		6.2	2.5	1.6
426		1.9	1.5	3.5
510		0.9	0.5	0

* Here c_0 is the initial ketal concentration.

As was to be expected from the Ruggli–Ziegler principle, as the initial acetophenone ketal concentration rises from 0.25 to 1.5 M, the content of macrorings diminishes and that of linear condensation products increases (Table 2).

The study of the temperature dependence of the yield of 1,3,5-triphenylbenzene showed that its maximum amount is formed at approximately 20°C.[21,23] An increase of temperature may prevent the formation of triphenylbenzene both due to the side reaction involving the addition of HCl to the vinyl ether group and in consequence of the decrease of the concentration of gaseous HCl in solution. The decrease of the yield at reduced temperatures can also be explained by factors other than the decrease of the reaction rate. It was found[23] that the kinetic curves for the formation of 1,3,5-triphenylbenzene below 20°C reach a limit and an increase of the duration of synthesis does not alter the yield of triphenylbenzene. The reduction of the temperature of the synthesis also leads to an increase of the inductive period. On the basis of these findings, the decrease of the yield is presumably associated with the difficulty of the formation at reduced temperatures of α-ethoxystyrene, which is formed spontaneously from the ketal at elevated temperatures. The fact that the yield of 1,3,5-triphenylbenzene is independent of whether the reaction is carried out in benzene solution presaturated with HCl or whether HCl is passed through the reaction mass during synthesis is of interest from the technological point of view[23].

In order to investigate the influence of the structure of the initial ketal on the cyclocondensation process, the ethyl ketals of 4-acetylbiphenyl, 4-acetylphenyl phenyl

ether, and 4′-acetyl-1,3,5-triphenylbenzene, as well as the butyl ketal of acetophenone were used[26,27]. At 20°C and with HCl passed through the system the reaction terminates after 25–30 min in all cases and its yield is fairly high (approximately 70%).[27] This may support the view that an increase of the number of benzene rings does not reduce the reactivity of the ketal. It is noteworthy that an increase of the number of benzene rings in the molecules of 1,3,5-trisubstituted oligophenyls reduces sharply their solubility. The introduction of a pivotal oxygen atom between the benzene rings greatly increases the solubility. The replacement of ethyl ketals by other alkyl ketals apparently has little effect on the nature of the cyclocondensation reaction[26].

The condensation of the acetophenone ketal in the range 100–400°C has also been studied[21,23]. Investigation by thin-layer chromatography of the condensation products obtained at 200°C in the presence of various catalysts showed that 1,3,5-triphenylbenzene is formed in the presence of acid catalysts. In the presence of alkaline catalysts and in the absence of a catalyst the condensation products contain only dypnone, α-ethoxystyrene, and the ketal which failed to react. The content of 1,3,5-triphenylbenzene in the reaction mass was estimated quantitatively by gas–liquid chromatography. The efficiency of the catalysts decreases in the sequence $TsOH.H_2O > H_2SO_4 > ZnCl_2 > SnCl_4$. An increase of the temperature of the synthesis leads to a decrease of the content of 1,3,5-triphenylbenzene in the reaction mass, while the overall yield of the condensation products is in all cases constant, i.e. the decrease of the yield of 1,3,5-triphenylbenzene is associated with the enhancement of the role of reactions leading to the formation of polyvinylenes[21].

Summarising the data for the cyclocondensation of the ketals of aryl methyl ketones, one may assume that the optimal conditions for the PCC of ketals obtain when the reaction catalysed by HCl is carried out in non-polar aromatic hydrocarbons at an initial concentration of the ketal groups of approximately 1*N* and at a temperature of 15–25°C or when the process is carried out at a higher temperature in the presence of $TsOH.H_2O$.

2. Characteristic Features of the PCC of Ketals

Taking into account the main features found with the aid of the model reaction, including the property of the PCC involving the possibility of a significant decrease of the solubility of polyphenylenes with increase of their molecular weight and gel formation, the synthesis of polyphenylenes was carried out in two stages[20]. Initially polyphenylenes with a relatively low molecular weight and residual reactive ketal or acetyl end groups were obtained in solution under the conditions of PCC; these fore-polyphenylenes were then converted, on heating under processing conditions (conversion into finished articles), into the final polymers with a cross-linked structure.

The use of the ethyl ketal of *p*-diacetylbenzene as the initial monomer in the reaction carried out in benzene in the presence of HCl as the catalyst leads to the formation of a cross-linked polymer in a quantitative yield[28]. In the first step of the interaction the branching of the polymer already begins and subsequently leads to the rapid formation of a network structure. It is quite understandable that the process should depend on the amount of HCl. It was found that, with increase of the rate of supply of HCl, the duration of synthesis before the attainment of the gel formation point diminishes; the overall consumption of the catalyst remains constant for the given charge in the reactor. This type of relation is associated with the rate of saturation of the solution by hydrogen chloride, which, up to a certain value, is directly proportional to the rate at which hydrogen chloride is passed. It was found[23] that an increase of the rate of supply of HCl within certain limits entails a directly proportional decrease of the time of attainment of the gel formation point. With increase of the charge severalfold, it is necessary to increase by the same factor either the duration of synthesis or the rate of supply of the catalyst. Thus the synthesis of the polymer may be regulated by controlling the amount of catalyst.

In order to obtain polymers with higher molecular weights in the first stage and to suppress the branching reaction, joint PCC of the ketals of mono- and di-acetyl compounds was carried out[28]. Fig. 1, which presents the dependence of the gel formation time and the amount of the gel fraction in the joint PCC of the acetophenone and *p*-diacetylbenzene ketals on their initial molar ratio, shows that, with increase of the fraction of the monofunctional monomer, the rate of gel formation falls and the proportion of the soluble fraction increases. For a molar ratio of 1 : 2, gel formation is not observed in the course of 2.5 h, but an increase of the amount of blocking agent leads to a decrease of the molecular weight of the polymer and of the amount of terminal functional groups, which is undesirable for the subsequent hardening stage. All the polyphenylenes synthesised in this way were therefore obtained mainly with an equimolar ratio of the mono- and bi-functional monomers.

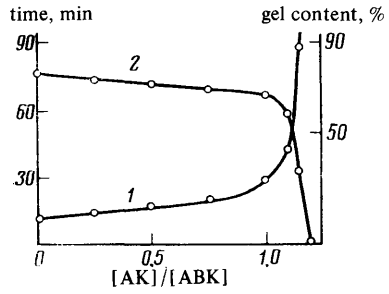


Figure 1. Dependence of the gel formation time (curve *1*) and of the amount of gel (curve *2*) in the PCC of the acetophenone ketal (AK) and the *p*-diacetylbenzene ketal (ABK) on their initial molar ratio.

In order to elucidate the nature of the PCC process, a thermodynamic study was made of the synthesis of polyphenylene from the ketals of acetophenone and *p*-diacetylbenzene[29,30]. The enthalpy of the process and the enthalpies of combustion and heat capacities of the monomers and polymers were determined. The enthalpies, entropies, and Gibbs free energies of formation of polyphenylene by PCC in solution and of its conversion into a three-dimensional polymer on heating were calculated from the results. Both processes are thermodynamically

allowed and their equilibria are almost completely displaced towards the formation of the corresponding polymer. Thus at 298.15 K the equilibrium constants K_e for the two reactions are respectively 1.5×10^{24} and 1.35×10^{5}. Thus the PCC of ketals in solution is known to be a non-equilibrium process, since, according to Korshak's definition[31], non-equilibrium processes are those for which $K_e > 10^3$.

The chain conjugation energy in the three-dimensional polyphenylene has been estimated[31]. Having assumed to a first approximation that the energy of the van der Waals interaction in this polymer is close to the analogous value in crystalline *m*-terphenyl, it was found that the chain conjugation energy is 62.5 kJ mole^{-1}, which agrees with the estimated chain conjugation energy in the polyphenylene obtained by the polycyclotrimerisation of phenylacetylene with *p*-diethynylbenzene[32].

Table 3. Kinetics of the PCC of the ethyl ketal of *p*-diacetylbenzene (20 °C, initial concentration 0.5 M, HCl concentration 0.2 M).

Time, min	Current ketal concn., M	k_1, litre mole^{-1} min^{-1}	k_2, litre mole^{-1} min^{-1}
0.35	0.225	1.96	—
0.5	0.201	1.90	—
0.65	0.177	2.02	—
0.75	0.164	2.03	—
1.0	0.151	2.03	—
2.0	0.127	—	0.172
3.0	0.119	—	0.177
4.0	0.115	—	0.198
5.0	0.113	—	0.162
7.0	0.104	—	0.171
10.0	0.096	—	0.192
		k_{av} = 1.99	k_{av} = 0.18

Taking into account the non-equilibrium nature of the PCC of ketals, the reaction kinetics were studied in benzene solution in the presence of dry HCl,[23,33-35] the aim being to elucidate the sequence of the interactions of the above monomers, to be able to achieve their optimal selection for the synthesis of polyphenylenes, and to elucidate the dependence of the reactivity of the monomers on their structure. The kinetics of the cyclocondensation and polycyclocondensation of the acetophenone, 4'-ethylacetophenone, 2-acetylfluorene, 4'-acetyl-1,3,5-triphenylbenzene, *p*- and *m*-diacetylbenzene, 4,4'-diacetylbiphenyl, and di-(4-acetylphenyl)methane ketals were studied. The cyclocondensation of the monoketals is a second-order reaction and its rate constants are close to the rate constant for the cyclocondensation of the acetophenone ketal, i.e. the rate of reaction is almost independent of the structure of the chosen monoketals. In contrast to this, the kinetics of the PCC of diketals, for example, the diketal of *p*-diacetylbenzene, involve two sharply differentiated regions (Table 3).[23] The rate constant in the second kinetic region shows no tendency to decrease and is an order of magnitude lower than in the first region. Data for other diketals are presented in Table 4.[33] They were calculated in addition by the method of Frost and Schwemer for parallel-consecutive reactions. The different reactivities of the functional groups (cf. No. 1 and No. 4 in Table 4) are associated with the activation of the carbonium ion formed from the first ketal group owing to the electron-accepting properties of the second group transmitted via the conjugation system of the benzene ring. Naturally the introduction of groups which interrupt the conjugation system or the absence of an *M*-effect in the *m*-position of the benzene ring lead to a value of k close to those of the rate constants for monofunctional compounds. Thus the properties of the initial ketal can influence the structure and properties of the polyphenylenes produced by the reaction. It has been shown[36] that, when the ketal of *m*-diacetylbenzene is used, the formation of high-molecular-weight polyphenylenes in PCC in solution is hindered by the formation of *m*-phenylene macrocyclic structures, the smallest of which should be a substituted cyclohexa-*m*-phenylene fragment. This nature of the process also explains the appreciable decrease of k_2 compared with k_1 in the PCC of the *m*-diacetylbenzene ketal (Table 4).

Table 4. The rate constants for the PCC of the ketals of aromatic acetyl compounds*.

No.	Initial compound	k_1, litre mole^{-1} min^{-1}	k_2, litre mole^{-1} min^{-1}	k'_1, litre mole^{-1} min^{-1}	k'_2, litre mole^{-1} min^{-1}
1	Ethyl ketal of *p*-diacetylbenzene	1.99	0.18	2.34	0.49
2	Ethyl ketal of *m*-diacetylbenzene	0.165	0.01	0.22	0.028
3	Ethyl ketal of di-(4-acetylphenyl)methane	0.16	—	0.175	—
4	Ethyl ketal of 4,4'-diacetylbiphenyl	1.2	0.5—0.7	1.73	**

*Rate constants calculated by the method of Frost and Schwemer are designated by k'_1 and k'_2.
**The value of k_2 for the polycyclocondensation reaction is approximately an order of magnitude lower than k_1.

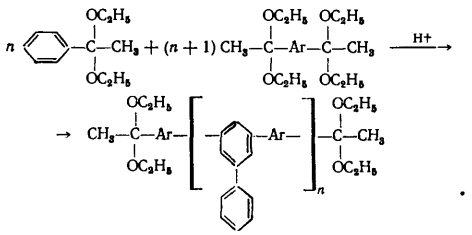
A study by infrared spectroscopy of the hardening of polyphenylenes at 350 °C in the presence of a catalyst showed[37] that it results in an increase of the number of 1,3,5-trisubstituted benzene rings, i.e. further trimerisation PCC of the end groups of the polyphenylene takes place.

The PCC of di- and mono-ketals can be carried out in such a way that polyphenylenes without reactive end groups are formed. For this purpose, one uses an excess of the mono-ketal, whose introduction leads simultaneously to chain termination. Thus when the *p*-diacetylbenzene ketal and a sixfold excess of the acetophenone ketal were used, an oligomer consisting mainly of a branched oligophenyl with 13 benzene rings was obtained. Judging from gel permeation chromatographic data (Fig. 2), the oligophenyl is identical with the model compound synthesised by the trimerisation cyclocondensation of the ketal of 4'-acetyl-1,3,5-triphenylbenzene[50].

3. The Synthesis of Polyphenylenes from Ketals Having Various Structures and Their Properties

If it is assumed that the reactivities of the ketals of mono- and di-acetyl compounds in PCC are close and in addition that there are no side reactions, the hypothetical linear polyphenylene (pre-polymer) should be obtained

for an equimolar component ratio. The syntheses were therefore carried out using equimolar ratios of the initial ketals. In this case the reaction can be represented schematically as follows:



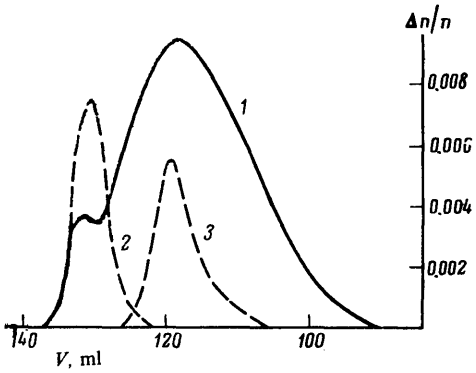
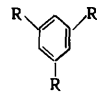


Figure 2. Gel permeation chromatography of the products of the PCC of the ketals of *p*-diacetylbenzene and acetophenone in molar proportions of 1 : 6 (curve *1*), 1,3,5-triphenyl benzene (curve *2*), and the oligophenyl



(curve *3*), where

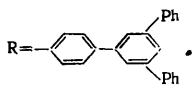
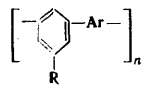


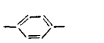
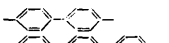
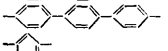
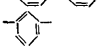
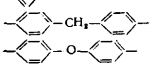
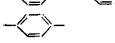
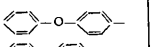
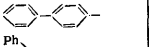
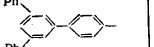
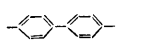
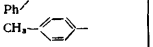
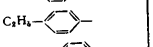
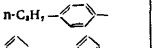
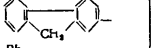
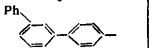
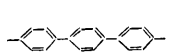
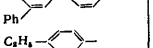
Table 5 presents certain properties of polymers based on the ketals of diacetylarylenes and acetophenone. The pre-polymers synthesised consisted of slightly coloured powders, readily soluble in ordinary organic solvents. The formation of a 1,3,5-trisubstituted benzene ring and the occurrence of the joint polycyclocondensation of the ketals of diacetylarylenes and acetophenone were confirmed by infrared spectroscopic data[37,40]. An increase in the content of *para*-substituted benzene rings in the main chain of the pre-polymer leads to a sharp decrease of the solubility of the polymer, while in the case of the ketal of 4,4″-diacetyl-*p*-terphenyl the pre-polymer is soluble only in nitrobenzene. The introduction of bridge groups such as –O– and $-CH_2-$ increases the mobility of the individual units of the molecule and reduces the softening temperature (Table 5), which is very important for the processing of the polymer. However, the introduction of the above connecting groups reduces the thermal stability of the final three-dimensional polymers obtained by the heat treatment of the fore-polymers.

The modification of the pre-polymers by altering the structure of the monofunctional monomer is of interest from this point of view[38,39] (Table 5). The pre-polymers synthesised in this way from the *p*-diacetylbenzene ketal are readily soluble. The highest solubility was observed in dichloroethane, dioxan, and chloroform. Comparison of the solubilities in toluene (Table 5) showed that the polymer with the most bulky side group, such as that derived from 1,3,5-triphenylbenzene, has the highest solubility.

Table 5. The properties of pre-polyphenylenes having the general formula

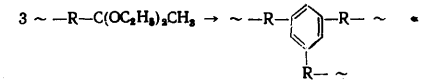


and based on the ketals of diacetylarylenes and monoacetyls.

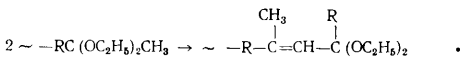
Structure of initial monomers		η_{int} in $CHCl_3$, dl g^{-1}	Solubility			Refs.
–Ar	R		in toluene (quantitative solubility, g $litre^{-1}$)	in $CHCl_3$	in nitrobenzene	
	Ph–	0.08	+ (14)	+	+	20, 28
	Ph–	0.07	–	+	+	20, 28
	Ph–	0.07*	–	–	+	22
	Ph–	0.14	+ (>200)	+	+	36
	Ph–	0.12	+	+	+	20, 28
	Ph–	0.08	+ (>200)	+	+	20, 28
		0.06	+ (30)	+	+	38
»		0.04	+ (33)	+	+	38
»		0.08	+ (50)	+	+	39
		0.14	+ (10)	+	+	39
»		0.25	+ (>200)	+	+	39
»		0.14	+ (>200)	+	+	39
»		0.11	± (2)	+	+	39
»		0.12	+ (10)	+	+	39
		0.09	+ (50)	+	+	35

*The measurements were made in nitrobenzene.

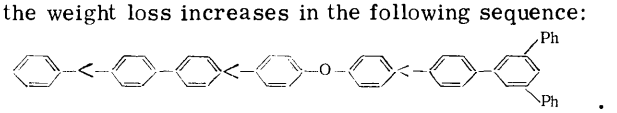
The pre-polymers synthesised were heat-treated in order to convert them into the final three-dimensional polymers with high thermal stability and heat resistance[20, 22,23,35]. The polymer may be cross-linked in two ways. Firstly, by the interaction of three end groups it is possible to form a new 1,3,5-trisubstituted benzene ring via the mechanism



Secondly, when two end groups interact, condensation may take place with formation of dypnone fragments and then polyvinylenes:



The second type of interaction leads to the appearance of defective fragments in the polymer structure. It was shown that the highest thermal stability and heat resistance are exhibited by fully aromatic polymers[23,28] or polymers with an aromatic main chain[38,39]. Thus a hardened polymer with the oxygen bridge group in the side chain begins to decompose at a temperature approximately 70°C higher than a polymer with the same group in the main chain. The study of the thermal degradation in an inert atmosphere of the polyphenylenes based on the *p*-diacetylbenzene ketal with various side groups showed that the weight loss increases in the following sequence:



This is apparently associated with the elimination of phenyl side groups.

Together with thermogravimetric analysis, the method involving pyrolysis in a closed volume with subsequent gas-chromatographic analysis of the volatile degradation product was used[23]. In order to discover to what extent the structure of the hardened products resembles that of polyphenylene, a study was made of the thermal stabilities of a number of model compounds containing 1,3,5-trisubstituted benzene rings[27]. The thermal degradation of the model compounds entails the liberation of hydrogen and methane alone, which are the main products of the decomposition of the benzene rings. The hardening of the prepolymers at 450°C gives rise to products in the pyrolysis of which hydrogen and methane are evolved in the same temperature range (>450°C) as for the model compounds. In the pyrolysis of the polymers hardened at 300°C hydrogen and methane appear at lower temperatures compared with the model compounds, which can be explained by the presence of end groups and defective fragments in the structure (Fig. 3).

Polymers based on the ketals of *p*-diacetylbenzene, 4,4′-diacetylbiphenyl, and 4,4″-diacetyl-*p*-terphenyl, hardened under optimal conditions, exhibit the highest thermal stability and heat resistance[23]. However, a disadvantage of these polyphenylenes is their low solubilities in the pre-polymer stage, which seriously limits their practical synthesis and in addition hinders polycyclocondensation to high degrees of conversion. The solution of the second problem, i.e. the synthesis of high-molecular-weight soluble polyphenylenes by one-stage PCC in solution, is undoubtedly a very attractive proposition, despite its entire potential complexity owing to the possibility of the formation of a network structure, since it would make it possible to extend the assortment of systems capable of practical utilisation. Several studies have been devoted to the solution of this problem[35,39,41].

The PCC of the *m*-diacetylbenzene ketal has been investigated[36,41] and polyphenylenes based on it have been synthesised. The choice of this monomer is dictated by the fact that, in view of the angular disposition of the benzene rings, *m*-polyphenylenes have a looser packing compared with *p*-polyphenylenes, which improves their solubility and lowers their melting point. However, the synthesis of high-molecular-weight polyphenylenes was hindered by the formation of macrocyclic *m*-phenylene fragments. The molecular weight (MW) characteristics and the molecular weight distribution (MWD) of the above polyphenylene have been studied[41]. Fractionation of the polymer led to the isolation of five fractions with $\overline{M}_w$ from 1400 to 115 000 and $\overline{M}_n$ from 1100 to 80 500. The MWD curves were plotted for each fraction in terms of the Shulz equation on the basis of the measured $\overline{M}_w$ and $\overline{M}_n$ for the fractions. The fore-polymer investigated has a fairly broad MWD and a coefficient of polydispersity of 7.6 (the coefficient calculated from the MWD curve is 7.3).

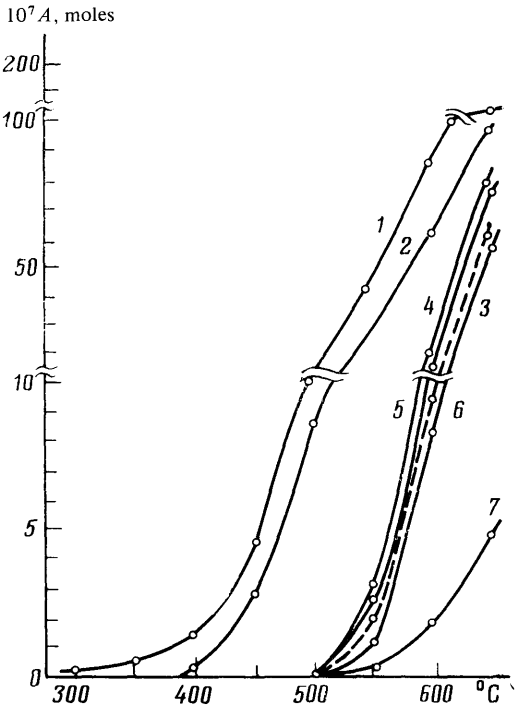
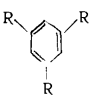
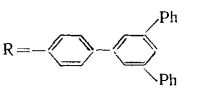


Figure 3. Methane evolution curves in the pyrolysis in a closed volume of the polyphenylene based on the *p*-diacetylbenzene and acetophenone ketals: 1) fore-polyphenylene; 2) fore-polyphenylene heat-treated at 300°C; 3) fore-polyphenylene heat-treated at 450°C; 4) the oligophenyl



where



5) 1,3,5-triphenylbenzene; 6) *m*-terphenyl.

Combined with a low intrinsic viscosity, this indicates a branched structure of the macromolecules. The coefficients of the Mark–Kuhn–Houwink equation for the first and second sections of the $\lg[\eta] - \lg\overline{M}$ relation were calculated and these too indicate a branched structure of

the polymers: $[\eta]_1 = 3.16 \times 10^{-4} \overline{M}_w^{0.6}$; $[\eta]_2 = 9.55 \times 10^{-4} \overline{M}_w^{0.22}$. For all the fractions, the increments in the refractive index and the specific partial volumes are similar. In other words, the degree of branching is similar for all the fractions. It is noteworthy that, for a comparatively low molecular weight of the initial pre-polymer, fractionation led to the isolation of a fraction with a fairly high molecular weight ($\overline{M}_w$ = 115 000). Unfortunately the proportion of this fraction proved to be very low, amounting to 2.5%.

The properties of polyphenylenes based on the ketal of 4,4′-diacetylbiphenyl, the most interesting monomer from the standpoint of its technological availability, and the thermal properties of the resulting polyphenylenes have been modified by synthesising copolymers with the *m*-diacetylbenzene ketal[36,39] and by introducing side groups into the polymer chain by altering the nature of the monofunctional monomer[38,39]. The introduction of *m*-phenylene fragments into the polymer chain was achieved by the joint PCC of the ethyl ketals of 4,4′-diacetylbiphenyl, *m*-diacetylbenzene, and acetophenone. The fore-polyphenylenes obtained were readily soluble in organic solvents, particularly when the initial mixture contained more than 75 mole % of the *m*-diacetylbenzene ketal. When mono-ketals having different structures were used (Table 5), it was found that the introduction of bulky substituents, for example, fluorene, triphenylbenzene, and diphenyl ether groups, causes only a slight alteration of the molecular weights and solubilities of polyphenylenes. In contrast to this, the introduction of alkyl substituents into the polymer side chain increases significantly the solubility and makes it possible to obtain polymers with a high molecular weight. For example, the PCC of the 4,4′-diacetylbiphenyl and *p*-ethylacetophenone ketals yields a fore-polymer with a viscosity of 0.25–0.30 dl g^{-1} and its $\overline{M}_w$ reaches 40 000–60 000; according to ^{1}H NMR data, the polyphenylene structure predominates in the polymer. This polymer is highly soluble in benzene and toluene in the cold (>200 g $litre^{-1}$).

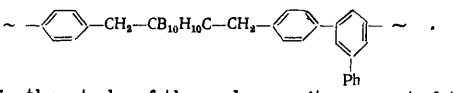
Table 6. The molecular weight characteristics of the fore-polymer based on the 4,4′-diacetylbiphenyl and *p*-ethylacetophenone ketals.

No. of fraction	Content, wt.%	$[\eta]$, dl g^{-1}	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	25.0	0.023	1 300	420	3.10
2	22.4	0.080	4 600	1 600	2.77
3	11.5	0.102	8 700	4 600	1.90
4	15.6	0.130	33 000	11 400	2.92
5	14.3	0.170	143 000	50 000	2.86
6	7.3	0.176	164 000	77 000	2.12
7	2.2	0.194	200 000	100 000	2.00
Initial fore-polymer	100.0	0.120	50 000	7 400	6.80

Polymers with ethyl side groups in the chain, pressed out at a high temperature, are hardly deformed up to the decomposition temperature (500 °C). In order to account for the causes of their very high thermal stability and heat resistance, a pre-polymer with blocked end groups was synthesised and its heat treatment yielded a highly thermostable product with a three-dimensional structure[39]. Consequently the ethyl group participates in the cross-linking process, which confirms the infrared spectroscopic data.

Thus the joint polycyclocondensation of *para*-substituted diketals with the *p*-ethylacetophenone ketal makes it possible to obtain polyphenylenes with a high solubility, a fairly high average molecular weight, and capable of being worked to form final articles with a high thermal stability. The study of the MWD of the pre-polyphenylene based on the ketal of 4,4′-diacetylbiphenyl and *p*-ethylacetophenone[35] demonstrated a fairly high polydispersity coefficient (6.8–9.9). The molecular weights of the polymer fractions isolated are listed in Table 6, which shows that, out of seven fractions, three have high molecular weights ($\overline{M}_w$ = 143 000–200 000), their overall proportion being 25%. The MWD within the fractions were calculated from the Schulz equation and their summation yielded the overall distribution curve for the non-fractionated polymer. The MWD curve proved to be fairly broad, which confirms the branched structure of the polyphenylene investigated. Thus the possibility, in principle, of synthesising high-molecular-weight polyphenylenes with a non-cross-linked structure by the polycyclocondensation of ketals was demonstrated.

Polymers obtained by the PCC of carbaborane-containing ketals have been described recently[18,19,42]. Using the ethyl ketals of di-(4-acetylbenzyl)-*m*-carbaborane and acetophenone, a polymer with the following tentative structure of the elementrary unit was obtained:



However, in the study of the polymer it was noted that the contribution of the trimerisation polycyclocondensation to the overall polycondensation process was much smaller than in previous cases. The polymer was highly soluble in organic solvents at the fore-polymer stage and exhibited a high thermal stability in the final stage, showing no weight loss on heating in air to 900 °C according to thermogravimetric analysis.

IV. PRACTICAL APPLICATIONS OF POLYPHENYLENES BASED ON AROMATIC ACETYL COMPOUNDS AND THEIR KETALS

Polymers based on aromatic acetyl compounds obtained by the method of Korshak et al.[5] are used to make fancy articles and filled plastics exhibiting a high thermal stability and heat resistance as well as resistance to corrosive media[5,43]. They are of interest as binders for the formation of antifriction polymeric materials[45]. The decrease of the coefficient of friction of the composition based on a carbon fabric takes place in parallel with the decrease of the rigidity of the polymer chain. Polymers based on ketals, obtained by the method of Korshak et al.[20], are also of interest for the formation of a wide variety of thermostable and heat resistant materials, particularly glass and carbon plastics[23,44]. The modification of these polymers by the introduction of sulphide bridges into the chain yielded materials with an enhanced mechanical strength without decrease of thermal stability[46,47].

The presence of organoelemental fragments in the chains of polyphenylenes imparts specific properties to the latter. Thus polymers based on di-(acetylbenzyl)-carbaboranes and their ketals[18,19] exhibit an exceptionally high thermal

stability. Glass plastics with a working temperature of 400°C have been made from them. The use of cobaltocenium-containing diacetyls and acetophenones made it possible to obtain thermostable anion-exchange resins[48].

A disadvantage of polyphenylenes based on aromatic acetyl compounds and their ketals from the standpoint of their practical application is the high temperature of their conversion into the final three-dimensional polymers. This problem is solved by replacing the acetyl groups in the fore-polymers, obtained by the trimerisation of PCC, by more reactive groups, for example furfurylidene, hydroperoxy-, or nitrile groups[35], as well as cyanomethyl cinnamate[49] and dicyanopropylidene[51] groups.

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Thus the use of the trimerisation PCC of aromatic acetyl compounds and their ketals not only expands our ideas about this process and about the dependence of the properties of polymers on their structure, but also makes it possible to obtain polymeric materials which are extremely valuable in practice.

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Oxidative Polymerisation of Vinyl Monomers

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The results of studies on the kinetics and mechanism of the oxidative polymerisation and copolymerisation of vinyl monomers are described systematically and discussed critically. Attention is concentrated on the elucidation of the relation between the structure and reactivity of the monomers in oxidative polymerisation and on the role of oxygen as an inhibitor in the free-radical chain polymerisation.
The bibliography includes 139 references.

CONTENTS

I.	Introduction	199
II.	Kinetics and mechanism of oxidative polymerisation	199
III.	Oxidative copolymerisation	204
IV.	Relation between the structure and reactivity of monomers	206
V.	Oxygen as an inhibitor of radical polymerisation	208

I. INTRODUCTION

Radical polymerisation in the presence of oxygen, called oxidative polymerisation †, is accompanied by oxidation which results in the formation of low-molecular-weight products with oxygen-containing functional groups (aldehydes, ketones, etc.) in addition to the copolymers with oxygen. The specific features and characteristics of the simultaneous occurrence of polymerisation and oxidation have been the subject of numerous investigations, which have led to the establishment (mainly during the last three decades) of oxidative polymerisation as an independent field of radical-chain polymerisation.

The study of the role of oxygen in radical polymerisation, begun by Lebedev[4] and Staudinger[5] and continued mainly by Medvedev[6], Bovey and Kolthoff[7], and Barns et al.[8], enabled Schulz and Henrici[2], Mayo et al.[9], and Kern[10], to establish the principal features of the mechanism of the oxidative polymerisation of compounds of the vinyl type ‡.

† The term "oxidative polymerisation" is used in the literature usually for the polymerisation of monomers (oligomers) in the presence of O_2 when initiation is achieved as a result of degenerate branching by peroxides (hydroperoxides)[1]. On the other hand, if the initiator is introduced from outside, and degenerate branching does not play a significant role in initiation, the process is called "inhibited polymerisation"[2] or "oxidation"[3]. We believe it to be more logical and rigorous in relation to the reaction mechanism to extend the term "oxidative polymerisation" to all instances of the polymerisation of unsaturated compounds in the presence of oxygen, regardless of the method of initiation.

‡ Compounds of the vinyl type, whose C–O bonds are activated by $\pi-\pi$ conjugation or by electron-donating or electron-accepting substituents [-CN, C(O)-, -C(O)-O, Cl,  , etc.] in the α-position relative to the double bond, are considered. Compounds containing the $CH_3-CH=CH-$, $CH_2=CH-CH_2-$, $CH_2-CH=CH$, and $CH_2=CH-CH$ structural units, in which the substituents in the α-position with respect to the relatively inactive C=C bond are the methyl, methylene, or methylidyne groups, exhibiting a weak electron-donating capacity, are included with allyl compounds[9,11,12].

Studies[13–16] were unable to determine the mechanism of the formation of hydroperoxide and the generation of oxidation chains for compounds of the allyl type. However, the formation of hydroperoxides is most probably only one of the reactions involving the formation of polymers from allyl compounds in the presence of oxygen. On the whole, this process has remained little studied for compounds of the allyl type.

During recent years, there has been a sharp increase of interest in polymerisation in the presence of oxygen. This is associated with the current development of fundamentally new methods for the formation of organic coatings using monomers[17,18] and also with the fact that oxidative polymerisation constitutes the basis for the formation of films of unsaturated compounds. The theoretical aspect of the study of the interaction between oxygen and unsaturated compounds involves the fundamental problem of the relation between the structure and reactivity of organic compounds in radical addition and substitution reactions.

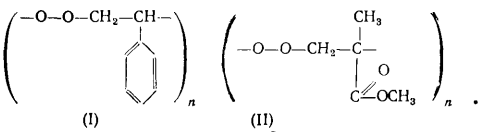
The available review publications are devoted mainly to the chemistry of polymeric peroxides[19–21] with the exception of a recent study in the field of the history of science[22], which reflects fairly completely the establishment of the field of oxidative polymerisation. It has now become necessary to survey and analyse critically studies dealing with the formation of polymers as a result of the interaction of unsaturated compounds with oxygen, to examine the present state of the field of oxidative polymerisation, to deduce the principle trends in its development, and to discover promising pathways to be followed in future research. Such an attempt is made in the present review.

II. KINETICS AND MECHANISM OF OXIDATIVE POLYMERISATION

1. Mono-unsaturated Compounds

Studies on the oxidative polymerisation of styrene[23–26], α-methylstyrene[27], and methyl methacrylate[2,3] have been of fundamental importance for the elucidation of the mechanism of the interaction of vinyl monomers with oxygen. The key to the understanding of the process mechanism has been the isolation[7,8,28] of polymeric peroxides derived

from styrene (I) and methyl methacrylate (II) and the determination of their structure as regular copolymers formed by the interaction of monomers with oxygen:

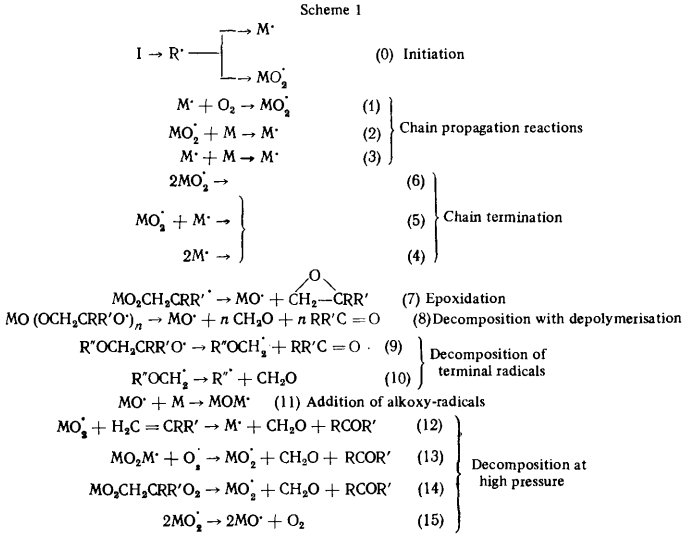


(I) (II)

It is noteworthy that Staudinger[29] was the first to identify a polymeric peroxide as the product of the interaction of 1,1-diphenylethylene with oxygen.

Styrene. The reaction of styrene with oxygen leads to the formation of a polyperoxide, benzaldehyde, formaldehyde, and styrene oxide (phenyloxiran), the aldehydes being formed in equimolar amounts simultaneously with the polyperoxide from the very lowest degrees of conversion[24,30]. The mechanism of the oxidative polymerisation of styrene [Scheme (1)], proposed by Mayo[25], provides a good explanation of the nature of the accumulation of the reaction products as a function of the partial pressure of oxygen (P_{O_2}) (see Figure). The polyperoxide and low-molecular-weight products are formed as a result of the addition, isomerisation, and decomposition of the radicals M$^{\cdot}$, $MO_2^{\cdot}$, and MO$^{\cdot}$ (I is the initiator).

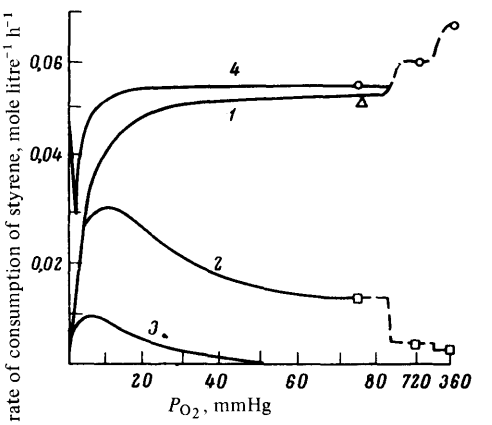
Scheme 1



The formation of the polymeric peroxide by reactions (0), (1), (2), and (6) in the range of oxygen pressures 160 to 3100 mmHg is consistent with kinetic results[24-26]. The rate of consumption of oxygen (W_{O_2}) obeys the equation

$$W_{O_2} = \frac{k_2}{k_6^{1/2}} \cdot k_i^{1/2} [M] [I]^{1/2} \qquad (I)$$

(where M, I, k_i, k_2, and k_6 are respectively the monomer, the initiator, and the initiation, chain propagation, and chain termination rate constants), which follows from the set of elementary reactions with the rate-limiting stage (2), indicated in scheme (1). In this oxygen pressure range W_{O_2} is independent of P_{O_2} and quadratic chain termination takes place at peroxy-radicals, the main reaction product is the polyperoxide, and the yield of low-molecular-weight compounds (phenyloxiran, CH_2O, and benzaldehyde) is approximately 3% (see Figure). Low-molecular-weight compounds are formed in the decomposition of radicals $MO_2^{\cdot}$ and $MO_2M^{\cdot}$ via reactions (11)-(14), whose rate is independent of P_{O_2}. Since $k_1/k_3 = 4.4 \times 10^6$ (at 50°C), all the radicals M$^{\cdot}$ are in fact converted into $MO_2^{\cdot}$ via reaction (1) before they can react with the monomer via reaction (3). The contribution of the MOOM$^{\cdot}$ radical decomposition reaction (7), which also competes with reaction (1), is small judging from the yields of the alkoxy-radicals and phenyloxiran at P_{O_2} = 3200 - 100 mmHg. Correspondingly the aldehyde formation reactions (8)-(10) do not play a significant role. This ensures the formation of the polyperoxide as the main product of the interaction of styrene and oxygen at $P_{O_2} \geq 100$ mmHg.



Dependence of the rates of formation of products in the oxidative polymerisation of styrene on the oxygen pressure[25]: *1*) polymeric peroxide; *2*) benzaldehyde and formaldehyde; *3*) phenyloxiran; *4*) overall rate of consumption of styrene; temperature -50°C; concentration of azobisisobutyronitrile 0.01 M.

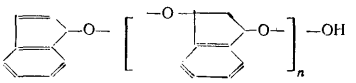
With decrease in the partial pressure of oxygen (particularly at P_{O_2} = 80 - 10 mmHg), the rate of formation of the polyperoxide diminishes and the yield of phenyloxiran and the aldehydes increases (see Figure). A decreased concentration of dissolved oxygen increases the lifetime of the radicals $MO_2M^{\cdot}$: $\tau = 1/k_1[O_2]$. This produces an increase in the rate of reaction (3) and in the rates of the isomerisation reaction (7) and the depolymerisation reactions (8)-(10), which gradually displace the polyperoxide formed. Since reaction (7) proceeds with an activation energy E_7 = 8-10 kcal mole^{-1}, [31] while reactions (1) and (3) which compete with it have $E_1 = 0$ and E_3 = 6-7 kcal mole^{-1}, [32] an increase of temperature causes, like a decrease of P_{O_2}, an increased yield of phenyloxiran and aldehydes compared with the formation of the polyperoxide. It has been shown[33] that under certain conditions {100-120°C, P_{O_2} = 160-80 mmHg, [M] = 10-40 vol.%} only oxidative-degradative reactions of styrene take place with formation of phenyloxiran and aldehydes, while the polymeric pathway in the interaction of styrene with oxygen is almost entirely suppressed.

When $P_{O_2} = 5-1$ mmHg, the cross-termination reaction (5) becomes dominant: $W_{O_2} \propto [M]^{1/2}[O_2]^{1/2}$: irregularities of the type ~M–M~, which hinder the depolymerisation reactions (8) and (9) and lower the yield of aldehydes, are encountered in polymer chains with increasing frequency. The rate of formation of phenyloxiran also decreases in view of the decrease of the fraction of ~MOOM~ units owing to the formation of ~MM~ and the overall rate of consumption of styrene falls sharply, since $k_5 \gg (k_4k_6)^{1/2}$. In the absence of oxygen ($P_{O_2} = 0$) polystyrene is formed by reactions (0), (3), and (4).

In terms of its most important features, the mechanism of oxidative polymerisation established for styrene proved to be valid for vinyl monomers such as α-methylstyrene[27,34-37] and methyl methacrylate[2,3,38,39].

Indene. The double bond activated by the aromatic ring and the methylene group in the α-position relative to the double bond are responsible for the ability of indene to interact with oxygen to form both hydroperoxides and polyperoxides[40,41]. Under mild conditions, the oxidation of indene leads to the formation of a hydroperoxide which is unstable above 40° C and is converted into carbonyl compounds[42].

Russell carried out a chemical and kinetic study of the oxidative polymerisation of indene[43,44], which established the structure of the polyperoxide:



and the mechanism of its formation via the reactions in Scheme 2.

Scheme 2

$$I \rightarrow R^{\cdot} \xrightarrow[M]{O_2} MO_2^{\cdot} , \quad (0)$$

$$M + O_2 \xrightarrow{k_{O'}} MO_2^{\cdot} , \quad (0')$$

$$M^{\cdot} + O_2 \xrightarrow{k_1} MO_2^{\cdot} , \quad (1)$$

$$MO_2^{\cdot} + M \xrightarrow{k_2} M^{\cdot} , \quad (2)$$

$$MO_2^{\cdot} + MH \xrightarrow{k_{2'}} MO_2H + M^{\cdot} , \quad (2')$$

$$2MO_2^{\cdot} \rightarrow \text{non-radical products.} \quad (6)$$

In contrast to styrene and methyl methacrylate, initiation reactions via the direct interaction of the monomer and oxygen [reaction (O')] and chain transfer reactions as a result of the elimination of hydrogen from the α-methylene group by the peroxy-radical [reaction (2')] play a significant role in the oxidative polymerisation of indene. The fact that the rate of the overall reaction obeys the equation

$$W_{O_2} = \frac{k_2 + k_{2'}}{k_6^{1/2}}[M](k_i[I] + k_{O'}[M])^{1/2}[O_2]^{1/2} \quad (II)$$

may be regarded as kinetic proof of the validity of the above scheme.

Thermal oxidative polymerisation has been investigated for styrene[23,45], methyl methacrylate[46], n-butyl methacrylate[47], and indene[44]. The rate of reaction obeys the equation

$$W_{O_2} = k[M]^n [O_2]^m \quad (III)$$

with values of n and m (Table 1) close to the theoretical values: $n = 1.5$ and $m = 0.5$. This enabled Mayor and Russell to assume that the reaction proceeds via Scheme 3, from which it follows that $k = k_i^{1/2}k_2/k_6^{1/6}$ in the above equation.

Scheme 3

$$M + O_2 \xrightarrow{k_{O'}} M^{\cdot} , \quad (0)$$

$$M^{\cdot} + O_2 \xrightarrow{k_1} MO_2^{\cdot} , \quad (1)$$

$$MO_2^{\cdot} + M \xrightarrow{k_2} M^{\cdot} , \quad (2)$$

$$2MO_2^{\cdot} \xrightarrow{k_6} \text{non-radical products.} \quad (6)$$

Chain initiation in vinyl compounds apparently proceeds as a result of the addition of oxygen to the double bond via the reaction[48,49]

$$C_6H_5CH{=}CH_2 + O_2 \rightarrow C_6H_5{-}\dot{C}H{-}CH_2OO^{\cdot} .$$

Table 1. Characteristics of oxidative thermal polymerisation of monomers.

Monomer	Reaction order w.r.t. monomer (n)	Reaction order w.r.t. oxygen (m)	Refs.	Monomer	Reaction order w.r.t. monomer (n)	Reaction order w.r.t. oxygen (m)	Refs.
Styrene	1.38	0.37	23	Indene	1.50	0.50	44
Styrene	1.78	0.34	45	Methyl methacrylate	1.70	0.47	46

The thermal oxidative polymerisation of styrene and n-butyl methacrylate at 50° C proceeds at rates smaller by a factor of 3–4 than in initiated oxidative polymerisation[23,45,47] owing to the low rates of initiation and degenerate branching of the chain by the polymeric peroxides.

In contrast to styrene, α-methylstyrene, methyl methacrylate, and indene, the oxidative polymerisation of other monomers of the vinyl type, such as chain-substituted[9,27,44] and ring-substituted[50] styrene, acrylonitrile[9,51-56] and its derivatives[54,57,58], methacrylates[39,59-64] and acrylates[46,57,63,65], vinyl acetate[9,57,66], and halogenoethylenes[67-76], has been studied much less. The kinetics of the interaction of oxygen with all the monomers investigated obey Eqn. (I). The influence of the medium is manifested by the fact that an increase in the dielectric constant of the solvent leads to an increase of the rate of reaction[59,60]. It follows from the kinetic data that the initiated oxidative polymerisation of compounds with activated π bonds proceeds via a mechanism incorporating the elementary reactions (0), (1), (2), and (6) (Scheme 1), in the region of oxygen pressures where the rate of reaction is independent of P_{O_2}. The copolymerisation of monomers with O_2, leading to the formation of polymeric peroxides, takes place via the chain propagation reactions (1) and (2) (Scheme 1). The comparatively few kinetic characteristics of the formation of polyperoxides are presented in Tables 2 and 3 (see also Table 6).

Table 2. Kinetic characteristics of the oxidative polymerisation of certain monomers.

Medium	Temp. °C	$10^3 k_2/k_6^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{1/2}$	$k_2/k_6^{1/2} = A \exp(-E/RT)$	Refs.
Styrene $CH_2=CHC_6H_5$				
Styrene	35	5.6	$k_2/k_6^{1/2} = 6.8 \cdot 10^4 \cdot \exp\left(-\frac{10\,000}{RT}\right)$	23*
	50	11.6		
	65	24.4		
Styrene	45	13.3	$k_2/k_6^{1/2} = 2.4 \cdot 10^3 \exp\left(-\frac{7700}{RT}\right)$	77
	50	16.5		
	55	18.8		
	60	22.8		
	70.5	32.0		
Styrene	35	6.8	$k_2/k_6^{1/2} = (5.8 \pm 0.3) \cdot 10^3 \cdot \exp\left(-\frac{8300}{RT}\right)$	46
	40	8.8		
	45	10.7		
	50	13.7		
	60	20.0		
α-Methylstyrene $CH_2=C(CH_3)-C_6H_5$				
Chlorobenzene	13	6.2	$k_2/k_6^{1/2} = (3.5 \pm 0.2) \cdot 10^2 \cdot \exp\left(-\frac{6170 \pm 300}{RT}\right)$	79
	30	13.0		
	40	15.5		
	50	23.0		
β-Methylstyrene $(CH_3)CH=CH-C_6H_5$				
β-Methylstyrene	50	5.65		27*
α-Phenylstyrene $CH_2=C-(C_6H_5)_2$				
α-Phenylstyrene	50	4.87		9*
		6.40		44*
β-Bromostyrene $CH(Br)=CH-C_6H_5$				
β-Bromostyrene	50	0.02		9*
Acrylonitrile $CH_2=CH-CN$				
Acrilonitrile	35	0.87	$k_2/k_6^{1/2} = (57 \pm 2) \cdot 10^3 \exp\left(-\frac{11\,000}{RT}\right)$	56
	40	1.21		
	45	1.62		
	50	2.20		
	55	2.75		
Substituted acrylonitriles $CH_2=C(R)-CN$ (in chlorobenzene)				
Methylacrylonitrile	50	4.60		54*
Ethylacrylonitrile	50	3.42		
n-Propylacrylonitrile	50	2.79		
Isopropylacrylonitrile	50	2.54		
n-Pentylacrylonitrile	50	2.44		
Methyl methacrylate $CH_2=C(CH_3)C(O)-OCH_3$				
Methyl methacrylate	30	0.61	$k_2/k_6^{1/2} = (17.4 \pm 1.0) \cdot 10^3 \cdot \exp\left(-\frac{10\,500}{RT}\right)$	39
	40	0.79		
	45	1.03		
	50	1.42		
	60	2.35		
n-Butyl methacrylate $CH_2=C(CH_3)C(O)-OC_4H_9$				
n-Butyl methacrylate	50	1.22	$k_2/k_6^{1/2} = (4.57 \pm 0.1) \cdot 10^4 \exp\left(-\frac{11\,200 \pm 800}{RT}\right)$	3
	65	2.56		
	80	5.30		
	35	0.60	$k_2/k_6^{1/2} = (6.7 \pm 0.5) \cdot 10^3 \cdot \exp\left(-\frac{10\,000}{RT}\right)$	39
	40	0.70		
	50	1.19		
	60	1.90		
n-Nonyl methacrylate $CH_2=C(CH_3)C(O)-O(CH_2)_8-CH_3$				
n-Nonyl methacrylate	50	1.32	$k_2/k_6^{1/2} = (33.9 \pm 9.0) \cdot 10^3 \cdot \exp\left(-\frac{11\,000}{RT}\right)$	39
	60	1.65		
	70	3.09		
	80	5.10		
n-Cetyl methacrylate $CH_2=C(CH_3)C(O)-O(CH_2)_{15}-CH_3$				
n-Cetyl methacrylate	50	1.08	$k_2/k_6^{1/2} = (6.4 \pm 0.7) \cdot 10^3 \cdot \exp\left(-\frac{10\,000}{RT}\right)$	39
	60	1.70		
	70	3.02		
	80	3.70		
	90	5.53		
Methyl acrylate $CH_2=CH-C(O)-OCH_3$				
Methyl acrylate	40	0.35	$k_2/k_6^{1/2} = (1.0 \pm 0.1) \cdot 10^3 \cdot \exp\left(-\frac{9400}{RT}\right)$	65
	50	0.42		
n-Butyl acrylate $CH_2=CH-C(O)-OC_4H_9$				
n-Butyl acrylate	50	0.47	$k_2/k_6^{1/2} = (0.18 \pm 0.02) \cdot 10^3 \cdot \exp\left(-\frac{8200}{RT}\right)$	65
	60	0.79		
	70	1.05		
	80	1.49		
n-Nonyl acrylate $CH_2=CHC(O)-O(CH_2)_8CH_3$				
n-Nonyl acrylate	50	0.42	$k_2/k_6^{1/2} = (1.36 \pm 0.10) \cdot 10^3 \cdot \exp\left(-\frac{9600}{RT}\right)$	46
	60	0.60		
	70	1.01		
	80	1.57		
Methyl vinyl ketone $CH_2=C-C(O)-CH_3$				
Methyl vinyl ketone	40	0.70	$k_2/k_6^{1/2} = (201 \pm 13) \cdot 10^3 \cdot \exp\left(-\frac{13\,500}{RT}\right)$	46
	45	1.07		
	50	1.38		
Vinyl acetate $CH_2=CHOC(O)-CH_3$				
Vinyl acetate	35	0.30	$k_2/k_6^{1/2} = (0.23 \pm 0.07) \cdot 10^3 \cdot \exp\left(-\frac{8300}{RT}\right)$	66
	40	0.41		
	45	0.51		
	50	0.61		
Tetrafluoroethylene $CF_2=CF_2$				
Water	40—70		$k_2/k_6^{1/2} = 65 \cdot \exp\left(-\frac{1200}{RT}\right)$	75
Indene 				
Indene	50	17.5		44
Phenylcyclohex-1-ene 				
Chlorobenzene	25	—	$k_2/k_6^{1/2} = 9.1 \cdot 10^3 \cdot \exp\left(-\frac{8400 \pm 300}{RT}\right)$	80, 81
	50	18		
	60	31		
	70	42		
	80	58		
Buta-1,3-diene $CH_2=CH-CH=CH_2$				
Butadiene	30	1.21	$k_2'/k_6^{1/2} = (10.3 \pm 1.1) \cdot 10^3 \cdot \exp\left(-\frac{13\,700}{RT}\right)$	82
	40	2.92		
	50	4.80		
Benzene	60	8.8		
Chloroprene $CH_2=CH-CCl=CH_2$				
Chloroprene	0	27.7	$k_2/k_6^{1/2} = 2.65 \cdot 10^3 \cdot \exp\left(-\frac{9600}{RT}\right)$	55
	20	92.8		
	35	207.6		

* The values of $k_2/k_6^{1/2}$ were calculated by the expression $k_2/k_6^{1/2} = W_{O_2}/[M]k_i[\bar{A}BIBN]^{1/2}$ from the rates of oxidative polymerisation W_{O_2} quoted in the relevant studies. The rate constants k_i for initiation by azobisisobutyronitrile (ABIBN) were taken from Tüdos[83] for styrene and its derivatives, from Turesanye and Tüdos[84] for vinyl acetate, from the same paper for acrylonitrile and its derivatives, from Sukhov and coworkers[46,85] for methacrylate and acrylate esters, from Turesanye and Tüdos[84] for methyl vinyl ketone, isopropenyl methyl ketone, and isopropenyl acetate, from Van Hook and Tobolsky[86] and Hammond et al.[87] for butadiene, and from Bailey[55] for chloroprene.

The structure of the polymeric peroxides corresponds to the formula -M-OO- when the monomer M reacts with oxygen under conditions (in terms of the O_2 concentration) ensuring quadratic chain termination by $\sim MO_2^{\cdot}$ radicals. The structure of the polymeric chains and peroxides with a regular alternation of -M- and -O-O- units constitutes independent confirmation of the validity of the mechanism of their formation under discussion. The extremely limited information about the structure of polymeric peroxides and some of their properties have been largely reviewed in Refs. 19–21 and 88.

Judging from the products formed, it is most likely that the thermal decomposition of the polymeric peroxides derived from styrene[24], α-methylstyrene[27], methyl methacrylate[38] n-butyl methacrylate[62], acrylonitrile[52], methacrylonitrile[53], vinyl chloride[68], and tetrafluoroethylene[73-75] proceeds via a free-radical chain mechanism.

In the oxidative polymerisation of vinyl compounds via the mechanism illustrated in Scheme 1 chain propagation takes place via the addition reaction (2). Together with addition to the double bond, the peroxy-radical can participate in the homolytic substitution reaction (2′) in Scheme 2, abstracting hydrogen from a monomer molecule. Polymeric peroxides, aldehydes, ketones, and epoxides are formed via the addition reaction[9], while hydroperoxides, alcohols, carbonyl compounds, and acids with the same number of carbon atoms as the initial olefin are formed via the substitution reaction[31,89]. On the basis of the study of the reaction products, Mayo et al.[9] concluded that the addition reaction predominates when the double bond is conjugated with aromatic, vinyl, carbonyl, or nitrile groups or when the saturated compound does not contain an allylic hydrogen atom. According to Buckley and Szwarc[90], the reactivity of unsaturated compounds as free radical acceptors increases sharply when their double bonds are activated by conjugation. Indeed, hydroperoxides or other substances indicating the occurrence of the substitution reactions have not been found in the products of the interaction with oxygen of all the compounds having activated π bonds investigated to date, with the exception of indene and phenylcyclohex-1-ene. It follows from the results of studies on the joint oxidation of styrene, α-methylstyrene, and methyl methacrylate with hydrocarbons such as tetralin and cumene (Tables 4 and 5) that peroxy-radicals add predominately to the double bonds.

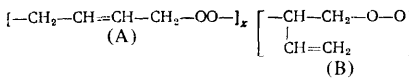
Thus the reaction involving substitution by the peroxy-radical plays a subsidiary role for vinyl compounds compared with the addition reaction. At the same time the kinetic chain is transferred to the monomer via the substitution reaction and the latter is probably largely responsible for the decrease of the length of the molecular chains of polymeric peroxides whose degree of polymerisation ($\bar{P}_n$) is as a rule comparatively low: $10 < \bar{P}_n < 30$.

Together with the competition between the substitution and addition reactions, the competition between the polymeric and oxidative pathways in the interaction of oxygen with monomers is extremely important. To date, this pathway has been studied only for styrene[25,31,33] and partly for α-methylstyrene[27,37] and methyl methacrylate[3,38].

2. Dienes and Polyenes

The mechanism of the oxidative polymerisation of hydrocarbons with conjugated double bonds has been established mainly as a result of the work of Kern and coworkers[92-95].

Buta-1,3-diene. The interaction of butadiene with oxygen in solvents gives a high yield of a polymer with $\bar{M}_n = 700-850$. This polymer is formed[96] as a result of the 1,2- and 1,4-addition of oxygen to butadiene, the latter pathway predominating:



(A) (B)

The structure of the polymer was demonstrated by its reduction with LiAlH to but-2-ene-1,4-diols and bute-3-ene-1,2-diols, the hydrogenation of which gave the corresponding butanediols. Formaldehyde and acrolein, identified in the thermal decomposition of the polymeric peroxide, corresponded to structure (B). Structure (A) was demonstrated by the formation of phenylhydrazones on treatment of the polymeric peroxide with phenylhydrazine.

Table 3. The rate constants for the elementary reactions in the oxidative polymerisation of certain monomers.

Medium	Temp., °C	k_2, litre mole^{-1} s^{-1}	$10^7 k_6$, litre mole^{-1} s^{-1}	k_2 (k_6) = $A \cdot \exp(-E/RT)$	References
Styrene					
Styrene	20	10.3	1.5		61
		9.9	1.8		
Chlorobenzene	13	19	4.8	$k_2 = (4.7 \pm 0.2) \cdot 10^7 \cdot \exp\left(-\frac{8400 \pm 300}{RT}\right)$	
	22	30	5.0		
	30	41	4.2		
	40	70	6.2	$k_6 = (1.04 \pm 0.20) \cdot 10^9 \cdot \exp\left(-\frac{1800 \pm 1200}{RT}\right)$	
	50	98	6.2		78
α-Methylstyrene					
α-Methylstyrene	20	2.2	0.015		61
Toluene		2.4	0.021		
Chlorobenzene	13	4	0.04	$k_2 = (6.6 \pm 0.7) \cdot 10^6 \cdot \exp\left(-\frac{8070 \pm 800}{RT}\right)$	
	30	10	0.06		
	40	15	0.08	$k_6 = (3.4 \pm 1.1) \cdot 10^8 \cdot \exp\left(-\frac{3700 \pm 1000}{RT}\right)$	79
	50	82	0.14		
β-Methylstyrene					
Chlorobenzene	30	51	3.2		79
Methyl methacrylate					
Methyl methacrylate	50	1.8	0.2	$k_2 = 8.3 \cdot 10^8 \cdot \exp\left(-\frac{12\,800}{RT}\right)$	63
	30	0.5	0.1	$k_6 = 2.1 \cdot 10^9 \cdot \exp\left(-\frac{4600}{RT}\right)$	
Methyl methacrylate	20	0.24	0.27	—	61
Methyl methacrylate	30	1.0	0.8	—	57
Butyl methacrylate					
Butyl methacrylate	30	0.8	0.3	$k_2 = 6.3 \cdot 10^7 \cdot \exp\left(-\frac{10\,900}{RT}\right)$	63
	50	2.8	0.4	$k_6 = 2.2 \cdot 10^8 \cdot \exp\left(-\frac{2600}{RT}\right)$	
Methyl acrylate					
Methyl acrylate	50	1.7	1.6	—	63
Butyl acrylate					
Butyl acrylate	50	1.4	9.0	—	63
Indene					
Chlorobenzene	30	128	5.0	—	79
Phenylcyclohex-1-ene					
Chlorobenzene	25	—	25		
	50	284	25		
	60	490	—	$k_2 = 1.4 \cdot 10^8 \cdot \exp\left(-\frac{8400 \pm 300}{RT}\right)$	80, 81
	70	664	—		
	80	915	—		

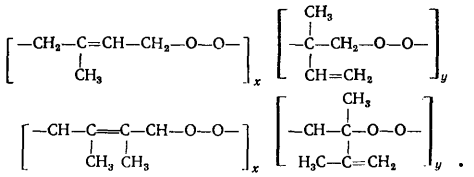
A detailed study of the initiated and thermal oxidative polymerisation of butadiene, undertaken by Mayo and coworkers[82,97], established that, in the temperature range 30–50°C, at $P_{O_2} > 40$ mmHg, and for low conversions, the main product is the polymeric peroxide $(C_4H_6O_2)_n$, consisting of equal numbers of *trans*-buta-1,2-diene and *trans*-buta-1,4-diene units connected by -O–O- bridges. Only at $P_{O_2} < 10$ mmHg is several per cent of 1-ethyloxiran (butadiene 1,2-oxide) and 1-formyloxiran (acrolein

1,2-oxide) formed. The epoxides are formed via reaction (7) in scheme 1, which had been established previously for styrene[25]:

$$\sim MO_2M^{\cdot} \xrightarrow{k_7} MO^{\cdot} + H_2C\overset{O}{\diagup\!\!\diagdown}CH{-}CH{=}CH_2 \ .$$

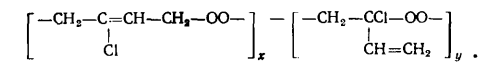
The rate of this reaction increases with decreased partial pressure of oxygen and the ratio k_1/k_7 is 3×10^{-6} and 20×10^{-6} at $P_{O_2} = 20$ and 3 mmHg respectively. The decomposition of polymeric alkoxy-radicals [reaction (8), Scheme 1] leads to acrolein: $\sim MO_2{-}MO^{\cdot} \rightarrow MO^{\cdot} + CH_2O + O{=}CH{-}CH{=}CH_2$; the radicals are formed via reaction (7) and have terminal buta-1, 2-diene units. The rate of initiation of the oxidative polymerisation of butadiene in the oxygen pressure range from 40 to 900 mmHg, where W_{O_2} is independent of P_{O_2}, obeys Eqn. (I) with the kinetic parameters listed in Table 2.

Isoprene and 2,3-dimethylbuta-1,3-diene. The available information about the interaction of oxygen with isoprene and 2,3-dimethylbuta-1,3-diene is extremely limited[92-94]. It has been shown[92-94] that the polymeric peroxides formed are regular copolymers of dienes with oxygen and have the following structure:

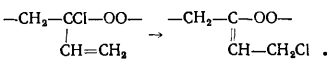


When the reaction of 2,3-dimethylbutadiene with oxygen is continued up to high conversions, hydroperoxy-groups and ether bonds appear in the polyperoxide, while α-isopropenylacrolein and dimethylglyoxal were detected in the volatile product in addition to formaldehyde and isopropenyl methyl ketone[98].

Chloroprene. The main product of the interaction of chloroprene with oxygen is a polymeric peroxide having the following structure[95,99]:



Readily hydrolysable chlorine, in amounts proportional to the amount of absorbed O_2, was detected in the polyperoxide. This led to the conclusion that oxygen undergoes 1,2-addition, which is accompanied, according to the authors[99], by the allylic rearrangement



A more detailed study of the structure of the polymeric chloroprene peroxide showed[55] that units resulting from 1,4-addition predominate. For low conversions, the kinetics of the oxidative polymerisation of chloroprene obey Eqn. (I). The principal kinetic characteristics of the process are listed in Table 2.

Thus, according to structural-chemical and kinetic data, polymeric peroxides of 1,3-dienes are formed via a mechanism incorporating the elementary reactions (0), (1), (2), and (6) (Scheme 1), the peroxy-radical adding to the monomer in the 1,4- and 1,2-positions.

The available information about the oxidative polymerisation of the *esters of acids having conjugated π bonds* is extremely limited. The addition of oxygen in the 1,2- and 1,4-positions of α-eleostearic acid has been demonstrated[100,101], the triene system of conjugated double bonds being converted into a diene system with formation of dimeric peroxy-products[102-104]. The peroxides derived from the methyl esters of octadeca-9,11-dienoic and octadeca-10,12-dienoic acids are regular 1 : 1 copolymers of the esters with oxygen whose degree of polymerisation is 2–4 [88] and which are formed as a result of the addition of polyperoxy-radicals in the 1,2- and 1.4-positions. The rate of oxidative polymerisation of the methyl esters of α-eleostearic[103] and octadeca-9,11-dienoic acids[93,105,106] obeys the equation

$$W_{O_2} = k\,[PP]^{1/2}.[M],$$

where [PP] and [M] are the concentrations of the polymeric peroxide and the monomer respectively.

This equation follows from Scheme 1 [elementary reactions (1),(2), and (6)], provided that the initiators are polyperoxides which decompose unimolecularly. The kinetics of the interaction of β-carotene (a polyene with conjugated π bonds) with oxygen were investigated and the formation of peroxides and epoxides in parallel reactions was established[107].

Table 4. The rate constants (litre $mole^{-1}s^{-1}$) for the reactions of certain peroxy-radicals with hydrocarbons at 30° C. [91]

Hydrocarbon	Peroxy-radical of				Average value for tertiary peroxy-radicals
	n-butane	*s*-butane	cyclohexane	tetralin	
Ethylbenzene	0.5	0.5	0.5	0.5	0.23
Cumene	0.4	0.4	—	0.5	0.17
Tetralin	6.4	4.2	4.5	6.3	1.7
Styrene	14	6.3	6.8	8.8	1.6
α-Methylstyrene	25	12	14	16	3.9*

* Data for cumenylperoxy-radicals.

III. OXIDATIVE COPOLYMERISATION§

The polymerisation process in a system consisting of monomers A and B and oxygen leads to the formation of ternary copolymers having the composition $(\sim AOO\sim)_n{-}(\sim BOO\sim)_m$. Chain propagation and termination proceeds via reactions in Scheme 4:

Scheme 4

$$\sim A^{\cdot}\,(\sim B^{\cdot}) + O_2 \rightarrow AO_2^{\cdot}\,(BO_2^{\cdot}) \qquad (1)$$

$$\left.\begin{aligned} \sim AO_2^{\cdot} + A &\xrightarrow{k_{AA}} \sim AOOA^{\cdot} \\ \sim AO_2^{\cdot} + B &\xrightarrow{k_{AB}} \sim AOOB^{\cdot} \\ \sim BO_2^{\cdot} + B &\xrightarrow{k_{BB}} \sim BOOB^{\cdot} \\ \sim BO_2^{\cdot} + A &\xrightarrow{k_{BA}} \sim BOOA^{\cdot} \end{aligned}\right\} \qquad (2)$$

$$\left.\begin{aligned} 2 \sim AO_2^{\cdot} &\xrightarrow{k_{OA}} \\ 2BO_2^{\cdot} &\xrightarrow{k_{OB}} \\ AO_2^{\cdot} + BO_2^{\cdot} &\xrightarrow{k_{OAB}} \end{aligned}\right\} \text{non-radical products.} \qquad (6)$$

§ By analogy with polymerisation in the absence of O_2, the term oxidative copolymerisation is applied when two and more monomers are involved in the polymerisation process.

Table 5. The constants for oxidative copolymerisation and co-oxidation of monomers*

Monomers and hydrocarbons	r_A	r_B	Φ	Temp., °C	Refs.
		Styrene (A)			
Butadiene	0.42±0.05	2.2±0.5	—	50	109
Butadiene	0.7±0.2	1.5±0.4	—	30	109
Butadiene	0.3±0.06	2.8±0.3	—	80	109
2,3-Dimethylbutadiene	0.37	2.75	—	50	109
α-Methylstyrene	0.48	2.1	6.2	50	9
α-Methylstyrene	0.9±0.1	1.2±0.1	—	60	110
α-Methylstyrene	1.6	0.71	—	70	111
Methyl methacrylate	7.9±1.0	0.078±0.0002	1.9÷1.1	50	9
Methyl methacrylate	3.6	0.28	0.8	60	112
Methyl methacrylate	9.2	0.09	—	50	113
p-Fluorostyrene	2.72	0.088	—	50	108
p-Fluorostyrene	0.89	0.98	—	50	108
p-Bromostyrene	0.88	0.97	—	50	108
p-Iodostyrene	0.705	0.995	—	50	108
p-Methylstyrene	0.71	1.51	—	50	108
p-Cyanostyrene	1.10	0.50	—	50	108
m-Nitrostyrene	1.24	0.32	—	50	113
p-Nitrostyrene	1.20	0.42	—	50	113
p-Nitrostyrene	1.50	0.22	—	60	114
p-Methoxystyrene	0.55	1.20	—	60	114
p-Methoxystyrene	0.38	2.10	—	50	113
Methyl sorbate	0.32	2.45	—	50	113
Methyl eleostearate	0.33	2.92	—	50	113
Tetralin	2.8±0.5	1.2±0.1	—	60	110
Tetralin	2.9	0.47		70	111
Tetralin	2.1	0.49	4.3	70	115
Tetralin	4.2	0.85	2.5	60	112, 116
Tetralin	2.3±0.3	0.43±0.03		60	117
Cumene	20±2	0.052±0.003		60	117
Cumene	6.5±1	−0.2±0.2	—	60	110
Cumene	13	0.1	10.5	60	112, 116
Cumene	18	0.045	—	70	111
Cyclohexene	1.2	0.15	8.7	60	112, 116
		p-Methoxystyrene (A)			
p-Nitrostyrene	2.3	0.17	—	60	114
		α-Methylstyrene (A)			
Methyl methacrylate	15±2	0.041±0.001	0.9–1.4	50	9
Tetralin	5.7	0.51	—	70	111
Cumene	9.3	0.1	—	70	111
		Butadiene (A)			
Tetralin	3.3±0.5	0.22±0.5	—	50	109
Cumene	23±3	0.03±0.01	—	50	109
s-Butylbenzene	25±10	—	—	50	109
Cyclopentene	1.8±0.5	0.58±0.07	—	50	109
Cyclohexene	4±1	0.10±0.03	—	50	109
Cycloheptene	3.0±0.1	0.38±0.02	—	50	109
Cyclo-octene	8±1	0.10±0.02	—	50	109
		Methyl methacrylate (A)			
Tetralin	0.6	2.9	1.7	60	112
Cumene	1.2	1.6	2.2	60	112
Cyclohexene	0.14	0.52	1.2	60	112

* The reaction was initiated in all cases by azobisisobutyronitrile and was carried out in bulk[9,108,111,112,115–117] or in solution[110,114] at P_{O_2} = 760 mmHg [108,110–112,115–117] or 3100 mmHg.[9]

If one of the system components is a saturated hydrocarbon BH, then oxidative copolymerisation is accompanied by joint oxidation:

$$\sim AO_2^{\cdot} + BH \rightarrow \sim AOOH + B^{\cdot},$$

$$\sim BO_2^{\cdot} + BH \rightarrow \sim BOOH + B^{\cdot}$$

with formation of terminal hydroperoxy-units in the polymer chains or of the hydroperoxide BOOH. It has been shown that the familiar equations for the composition of the copolymer and the general equation for the rate of reaction in three-component systems (the case where one of the monomers is incapable of homopolymerisation) are applicable to the oxidative copolymerisation of two monomers[9,108]. The relative chain propagation rate constants $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$ as well as the ratio of the rate constants for chain termination $\Phi = k_{OAB}(k_{OA}k_{OB})^{1/2}$ can be determined from these equations. The quantity r expresses the selectivity of the peroxy-radicals with respect to the monomers (the ratio of the rates of addtion to its "own" and "foreign" monomers), while the constant Φ represents the difference between the rates of chain termination as a function of the type of reacting peroxy-radicals.

The oxidative copolymerisation and co-oxidation constants for the monomers are listed in Table 5. The small number of publications and the extremely limited number of systems investigated are striking. A comparison of the results obtained by different workers is possibly only for the systems styrene–α-methylstyrene–O_2, styrene–methyl methacrylate–O_2, styrene–tetralin–O_2, and styrene–cumene–O_2. The reason for this is primarily the considerable experimental difficulties associated with a sufficiently accurate determination of the composition of polymeric peroxides, or with the measurement of the concentration of the monomer in the substrate undergoing oxidation[115,117].

Table 6. The chain propagation and termination rate constants for certain vinyl monomers*

R	monomer	$10^3 k_2/k_6^{1/2}$, litre$^{-1/2}$ mole$^{-1/2}$ s$^{-1/2}$ 50° C	$10^3 k_2/k_6^{1/2}$, litre$^{-1/2}$ mole$^{-1/2}$ s$^{-1/2}$ 30° C	k_2, litre mole^{-1} s^{-1} (30°C)	$10^{-7}k_6$, litre mole^{-1} s^{-1} (30°C)
	CH_2 = CHR monomers				
—CH=CH_2	Butadiene	11.9	—	—	—
—C_6H_5	Styrene	13.7	6.3	4.1	4.2
—CN	Acrylonitrile	2.20	0.47	3.3	6.0
—C(O)—CH_3	Methyl vinyl ketone	1.38	—	—	—
—C(O)—OCH_3	Methyl acrylate	0.42	0.14	0.6	1.7
O—C(O)—CH_3	Vinyl acetate	0.61	0.35	2.4	4.9
	$CH_2 = C(CH_3)-R$ monomers				
—CH=CH_2	—	—	—	—	—
—C_6H_5	α-Methylstyrene	23.0	13.0	10	0.06
—CN	Methylacrylonitrile	4.60	1.50	4.5	0.93
—C(O)—CH_3	Isopropenyl methyl ketone	2.22	—	—	—
—C(O)—OCH_3	Methyl methacrylate	1.42	0.48	0.5	0.10
O—C(O)—CH_3	Isopropenyl acetate	0.24	0.16	0.2	0.16

* The Table was set up on the basis of published data for butadiene[109], styrene[46,77], acrylonitrile[56,57], methyl vinyl ketone[46] methyl acrylate[56,65], vinyl acetate[56,66] α-methylstyrene[79], methylacrylonitrile[54,56], isopropenyl methyl ketone[54], methyl methacrylate[39,63], and isopropenyl acetate[54,56].

For all the pairs investigated, if $r_A < 1$ then $r_B > 1$ and, conversely, when $r_A > 1$ then $r_B < 1$ (Table 5), i.e. peroxy-macroradicals react predominantly with one of the monomers. The growing peroxide chains add to the "foreign" monomer ($r_A < 1$, $r_B < 1$) only in the oxidative copolymerisation of styrene with *p*-chloro-, *p*-bromo-, or *p*-iodo-styrene. When the comonomers of styrene and oxygen are compounds having conjugated double bonds (butadiene, 2,3-dimethylbutadiene, methyl sorbate, or methyl eleostearate), or α-methylstyrene, then the peroxy-macroradicals react preferentially with these compounds and

not with styrene. On the other hand, in the system butadiene (styrene)–O_2–tetralin (cumene or other hydrocarbons) the addition of peroxy-radicals is always much faster than the rate at which they abstract hydrogen.

The product $r_A r_B \simeq 1$ in the system styrene-butadiene–O_2, styrene-2,3-dimethylbutadiene–O_2, styrene–α-methylstyrene–O_2, and styrene (butadiene)–hydrocarbon–O_2. The product can serve as a measure of the selectivity of peroxy-radicals, because $k_{AB} = k_{BB}$ and $k_{AA} = k_{BA}$ when $r_A r_B = 1$. In the above systems each monomer exhibits approximately the same reactivity in relation to the radicals $AO_2^{\cdot}$ and $BO_2^{\cdot}$, while the reactivities of peroxy-radicals of both types differ insignificantly and depend little on the structure of their penultimate unit A or B. The absence of selectivity in relation to radicals is responsible for the disordered arrangement of the ~BOO~ and ~AOO~ units in the polyperoxide chains.

IV. RELATION BETWEEN THE STRUCTURE AND REACTIVITY OF MONOMERS[88]

The monosubstituted vinyl monomers investigated, which have the structure $CH_2 = CHR$, can be arranged in the following sequence in terms of increasing $k_2/k_6^{1/2}$: methyl acrylate ≃ vinyl acetate < methyl vinyl kentone < acrylonitrile < styrene < butadiene (series I) (Table 6). The corresponding series II formed by 1,1-disubstituted monomers having the structure $CH_2 = C(CH_3)R$ is: isopropenyl acetate < methyl methacrylate < isopropenyl methyl ketone < methylacrylonitrile < α-methylstyrene (Table 6). The chain propagation rate constants k_2, the absolute values of which exert a decisive influence on $k_2/k_6^{1/2}$, increase in the same sequence.

Table 7. The relative reactivities of the monomers ($1/r$) towards the polymeric radicals ~$MO_2^{\cdot}$ and ~$M^{\cdot}$ *

Monomer	~$MO_2^{\cdot}$ radicals (50°C) from				~$M^{\cdot}$ radicals (60°C) from		
	butadiene	α-methyl-styrene	styrene	methyl metha-crylate	butadiene	styrene	methyl methacryl-ate
Butadiene	1.0	—	2.4	—	1.0	—	4.0
α-Methylstyrene	—	1.0	2.1	25	—	0.85	2.0
Styrene	0.46	0.48	1.0	13	0.72	1.0	2.0
Methyl methacrylate	—	0.07	0.13	1.0	—	2.0	1.0

* The Table was set up on the basis of published data for oxidative copolymerisation[9,109,117] and copolymerisation[118].

However, comparison of the values of k_2 yields only a general idea about the efficiency of the elementary addition step for different monomers, since the absolute rate constants depend on the reactivity of both the monomer and the polyperoxy-radical. In order to discover which of the above factors is of decisive importance in oxidative polymerisation, it is necessary to find out how the reactivity of the monomers and the peroxy-radicals varies in the series under consideration. Judging from the form of variation of the reciprocals of the copolymerisation rate constants $1/r$ (Table 7) and the chain propagation rate constants (Tables 4 and 8), the reactivity of monomers as peroxy-radical acceptors increases in the following sequence: methyl methacrylate < styrene < α-methylstyrene < butadiene. For the remaining compounds in series I and II, there is no information about $1/r$ and $k_{AB}(k_{BA})$. This makes it necessary to infer the reactivity of the monomers from the rate of addition of the polymeric radicals ~$M^{\cdot}$ and not ~$MO_2^{\cdot}$, assuming that the monomer activity series do not then change significantly. This assumption may be resorted to on the basis of the concordant results obtained for butadiene, α-methylstyrene, styrene, and methyl methacrylate as regards the rates at which they accept the ~$M^{\cdot}$ and ~$MO_2^{\cdot}$ radicals (Table 7). According to copolymerisation data[118,120], the reactivity of monomers with respect to the radicals ~$M^{\cdot}$ varies in the following way: vinyl acetate < methyl acrylate < acrylonitrile < methyl vinyl ketone < styrene < butadiene (series III) and isopropenyl acetate < methyl methacrylate < methylacrylonitrile < α-methylstyrene (series IV).

According to the available extremely limited data (Table 8), the reactivity of peroxy-radicals ~$MO_2^{\cdot}$ derived from the monomers in reactions involving addition to a double bond decreases in the sequence: styrene > methyl methacrylate > α-methylstyrene. One should also note that secondary peroxy-radicals are more reactive than tertiary radicals not only in the hydrogen abstraction reaction[91], but also in addition to the double bond (Table 8) and in recombination steps (Table 3).

Table 8. The rate constants (litre $mole^{-1}s^{-1}$) of reactions of the ~$MO_2^{\cdot}$ and ~$M^{\cdot}$ polymeric radicals with monomers*

Monomer	~$MO_2^{\cdot}$ radicals (50°C) from			~$M^{\cdot}$ radicals (60°C) from	
	styrene	methyl-metha-crylate	α-methyl-styrene	styrene	methyl-methacrylate
α-Methylstyrene	204	43	28	—	1050
Styrene	98	23	13	170	1050
Methyl methacrylate	12	1.8	1.8	310	520

* The rate constants for the ~$MO_2^{\cdot}$ radicals were calculated from the values of r_A and r_B (Mayo et al.[9]) and from k_2.[63,78,79] Those for the ~$M^{\cdot}$ radicals were calculated from r_A and r_B (Ham[118]) and from k_3.[32,119]

The identical arrangements of the monomers in sequences I and III and II and IV support the conclusion that the main factor in oxidative polymerisation, which determines the overall rate of the process, is the reactivity of the monomers and not peroxy-radicals. This conclusion is consistent with the earlier hypothesis that the activity of the double bond plays a decisive role in oxidative polymerisation[9].

A rigorous justification of the above relation can be achieved at the present time only for α-methylstyrene and methyl methacrylate. ¶ In the oxidative polymerisation of these monomers the increase of $k_2/k_6^{1/2}$ and k_6 on passing

¶ In the oxidative copolymerisation of α-methylstyrene with styrene and of methyl methacrylate with styrene the products are tertiary and secondary peroxy-radicals respectively, having significantly different reactivities, which hinders a rigorous interpretation of the type of variation of $k_2/k_6^{1/2}$ and k_2.

from α-methylstyrene to methyl methacrylate parallels the increased reactivity of the monomers and is in opposition to the decreased reactivity of the radicals.

The increase of the rate of homopolymerisation of vinyl monomers is known to be equal to the increase in the reactivity of the corresponding macroradicals[32]. The inversion of this relation in oxidative polymerisation must be attributed to the nature of the chain-carrier radical resulting from the conversion of ~M· into $MO_2^·$ via the reaction ~M· + O_2 → ~$MO_2^·$. A direct comparison of the reactivities of the polymeric radicals ~M· and ~$MO_2^·$ is at present possible only for styrene and methyl methacrylate, because the required data are lacking for the remaining monomers.

Table 9. The rate constant ratios k_3/k_1 and the rate constants for the reaction ~M· + O_2 $\xrightarrow{k_1}$ ~$MO_2^·$ (at 50°C)*

Radical	Medium	$10^6 k_3/k_1$	k_1, litre mole^{-1} s^{-1}	Refs.
$-CH_2-\dot{C}H-CH=CH_2$	Butadiene	7.0±2.5	$1.0\cdot10^7$	82
$-CH_2-\dot{C}H-C_6H_5$	Styrene	3.7±0.4	$3.3\cdot10^7$	24
	Styrene	1.8	$6.6\cdot10^7$	25
	Styrene-benzene	⩽70	$1.7\cdot10^6$	26
$-CH_2-\dot{C}(CH_3)-C(O)-OCH_3$	Methyl methacrylate	50±3 0	$7.2\cdot10^6$	3
	Methyl methacrylate-benzene	⩽30	$1.2\cdot10^7$	2

* The values of k_3/k_1 were determined[3,24,25,82] from the results of the analysis of the composition of polymeric peroxides. The values of k_3/k_1 were estimated[3,26] from the results of the study of the overall kinetics of the polymerisation reaction. The rate constants k_1 were calculated with k_3 = 70, 120, and 360 litre mole^{-1}s^{-1} for butadiene, styrene, and methyl methacrylate respectively[32].

The peroxy-radical derived from methyl methacrylate is less active in the addition to the double bond than the peroxy-radical derived from styrene, while the opposite relation is observed for the ~M· radicals derived from the same monomers (see Table 8 and Bagdasar'yan's book[32], p.207). The reactivities of the ~M· and ~$MO_2^·$ radicals can be compared directly for each monomer in terms of the chain propagation rate constant ratio k_3/k_2 †. In this case the monomer from which the radicals have been derived serves for them as a comparison standard:

$$\sim M^· + M \xrightarrow{k_3} \sim MM^· \text{ and } \sim MO_2^· + M \xrightarrow{k_2} MO_2M^·.$$

The conversion of the radical ~M· into ~$MO_2^·$ is as a rule associated with a sharp decrease in the reactivity of the radical towards addition to the double bond, the decrease being more pronounced the more reactive was the radical ~M· (Table 10). The validity of this rule for all peroxy-radicals in the monomer series I and II should have the inevitable consequence that the decisive factor in oxidative polymerisation becomes the reactivity of the monomers and not the radicals. The levelling of the reactivities of the radicals on passing from ~M· to ~$MO_2^·$ is most probably caused by the significant decrease in the influence of the structure of the M monomer molecule on the reactivity of a free radical of the type ~$MO_2^·$ compared with a radical of the type M·. This influence does not apparently extend beyond the oxygen atom of the ~$MO^·$ fragement of the ~MOO· unit, because the directions of the orbitals of the lone electron pairs of the oxygen atoms in the -O-O- peroxy-groups are mutually perpendicular[121]. This is probably also the cause of the comparatively small change in the reactivity of primary, secondary, and tertiary radicals $RO_2^·$ in the abstraction of hydrogen atoms as a function of the structure of R [91,122,123] (Table 4).

† k_3/k_2 can be estimated from the ratio $k_3/k_4^{1/2} : k_2/k_6^{1/2}$, because $k_4^{1/2} = k_6^{1/2}$ (to within an order of magnitude).

Table 10. The rate constants for the polymerisation and oxidative polymerisation reactions of certain monomers (at 50°C)*

Monomer	$10^3 k_6/k_6^{1/2}$, litre mole^{-1} s^{-1}	$10^3 k_3/k_4^{1/2}$, litre mole^{-1} s^{-1}	γ	k_2, litre mole^{-1} s^{-1}	k_3, litre mole^{-1} s^{-1}	γ'
Styrene	13.7	15.0	1.1	98	120	1.2
Acrylonitrile	2.20	61.0	28	—	—	—
Methyl methacrylate	1.42	79.3	56	1.8	360	200
Vinyl acetate	0.61	264	430	—	—	—
Methyl acrylate	0.43	510	1200	1.7	980	570

* The values of $k_2/k_6^{1/2}$ and k_2 were obtained from the published data for styrene[46,77], acrylonitrile[56], methyl methacrylate[81,82], vinyl acetate[57,66], and methyl acrylate[57,65]. The values of $k_3/k_4^{1/2}$ and k_3 were evaluated from data of Bagdasar'yan[32]. Notation: $\gamma = k_3/k_4^{1/2} : k_2/k_6^{1/2}$; $\gamma' = k_3/k_2$.

The arrangement of the monomers in series I and II shows that the influence of substituents in these compounds on their reactivity decreases in the sequence $-CH_2=CH_2 \simeq C_6H_5- > -CN > -C(O)-CH_3 > -C(O)-OCH_3 \simeq OC(O)-CH_3$. In radical addition reactions of the same type the influence of substituents is interpreted on the hypothesis of a linear relation between the change in activation energy and the conjugation energy in the reacting molecules and radicals[32,124]. This approach is also possible in oxidative polymerisation. Allowance for other factors (apart from conjugation) capable of influencing the radical reactivity is at the present time still fairly difficult[125,126]. The treatment of the reactivities of monomers in oxidative polymerisation from the standpoint of the influences which the substituents exert on the electron density in π bonds is also acceptable. Calculations of the distribution of electron density in monomers[127,128] showed that the π-electron density in double bonds decreases in the sequence styrene > acrylonitrile > methyl methacrylate > methyl acrylate > vinyl acetate. Thus there is a correspondence between the change in the reactivity of the monomers in oxidative polymerisation and the electron density in their π bonds. This feature is consistent with the electron-accepting properties of peroxy-radicals[9,129].

Judging from the values of $k_2/k_6^{1/2}$ and k_2, unsaturated 1,1-disubstituted compounds having the structure $CH_2 = C(CH_3)R$ as a rule interact with oxygen at higher rates than the corresponding monosubstituted compounds $CH_2 = CHR$ (Table 6). The decrease of k_6 from 3×10^7 litre mole^{-1}s^{-1} to 7×10^5 litre mole^{-1}s^{-1} (at 50°C) makes a significant contribution to the increase of the ratio $k_2/k_6^{1/2}$ for α-methylstyrene relative to styrene, which compensates the

decrease of k_2 (Tables 2 and 3). However, the introduction of a more bulky substituent in the α-position relative to the double bond (for example in α-phenylstyrene) also leads to a decrease of $k_2/k_6^{1/2}$ (Table 2). The introduction of an electron-accepting substituent in the β-position reduces sharply the rate of oxidative polymerisation: β-bromostyrene reacts with oxygen at a rate smaller by two orders of magnitude than styrene or β-methylstyrene (Table 2). The introduction of electron-donating substituents (CH_3, CH_3O, etc.) in the *para*-position in the styrene ring increases the reactivity of the monomers, while electron-accepting substituents (F, NO_2) reduce it significantly (Table 5).

The rate of oxidative polymerisation of α-substituted derivatives of acrylonitrile varies as follows: methylacrylonitrile > ethylacrylonitrile > n-propylacrylonitrile > isopropylacrylonitrile > n-pentylacrylonitrile (Table 2). The hyperconjugation effect, arising owing to the interaction of the σ electrons of the C–H bonds of the substituents with the π electrons of the $H_2C = C(R)-C \equiv N$ conjugated system, probably increases in the above sequence, lowering the electron density in the double bond.

It has been established[46,63] that the quantity $k_2/k_6^{1/2}$ and correspondingly the rates of interaction of monomeric methacrylates and acrylates with oxygen, as well as the chain propagation rate constants k_2 depend only slightly on the size of the substituent R in the alkoxy-group in the esters $CH_2 = C(R_1)C(O)OR$, where $R_1 = H$ or CH_3 and R = CH_3, C_4H_9, C_9H_{19}, or $C_{16}H_{33}$ (Tables 2 and 3). It is most likely that the substituent R has no significant influence on the reactivity of the double bonds in the peroxy-radicals of acrylates and methacrylates. The double bonds in methacrylate esters are more reactive than those in acrylate esters in the addition reactions of both M$^{\cdot}$ [32] and $RO_2^{\cdot}$ [46] radicals. Presumably secondary peroxy-radicals having the structure $-CH_2-CH(R)(O)O^{\cdot}$ are more reactive than the tertiary radicals $-CH_2-C(R)(CH_3)OO^{\cdot}$ not only in the recombination reaction (Table 6) but also in the addition reaction. The opposite variation of the reactivities of the double bonds and free radicals should lead to the mutual approach of the values of k_2 for acrylates and methacrylates.

V. OXYGEN AS AN INHIBITOR OF RADICAL POLYMERISATION[88]

Oxygen is known to be an inhibitor of the polymerisation of vinyl monomers[2,32,130]. Saturation of the monomers with oxygen (air) reduces the rate of polymerisation and leads to the appearance of an inductive period. Inhibition takes place as a result of the highly efficient chain transfer of oxygen via the raction $\sim M^{\cdot} + O_2 \longrightarrow MO_2^{\cdot}$ and slow regeneration of the chain by peroxy-radicals: $\sim MO_2^{\cdot} + M \longrightarrow \sim MO_2M^{\cdot}$, because the rate of addition of the radical $\sim MO_2^{\cdot}$ to the double bond is much smaller than the rate of chain propagation: $\sim M^{\cdot} + M \longrightarrow \sim MM^{\cdot}$.

The available data make it possible to consider the mechanism of the inhibiton process and to observe the relation between the reactivity of monomers and the efficiency of the action of oxygen on radical-chain polymerisation.

Oxygen combines very rapidly with free radicals having an unpaired electron on a carbon atom, which serve as chain carriers in radical-chain polymerisation. The values of k_1 for the radicals M$^{\cdot}$ derived from butadiene, styrene, and methyl methacrylate lie in the range $2 \times 10^6 - 7 \times 10^7$ litre mole^{-1}s^{-1} (at 50° C) and depend little on the structure of the radical (Table 9). In general, the characteristic values of the rate constants k_1 for the reaction $R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot}$ are 10^6-10^8 litre mole^{-1}s^{-1}.[119] Judging from the values of k_1 quoted, oxygen reacts with free radicals of the type $R_1R_2R_3C^{\cdot}$ at the same rate as a free radical (typical values of k_4 and k_6 for the recombination reaction $2 \sim M^{\cdot} \xrightarrow{k_4}$ and $2RO_2^{\cdot} \xrightarrow{k_6}$ are 10^6-10^7 litre mole^{-1}s^{-1} [32,119]). This behaviour of oxygen can be accounted for by the characteristics of the electronic structure of its molecule. Oxygen in its ground electronic state is a biradical which has a $\sigma-\pi-\pi$ bonding skeleton and in addition two electrons with parallel spins in antibonding molecular orbitals.[131,132]

The ratio of the rates of the competing chain propagation reactions $\sim M^{\cdot} + M \xrightarrow{k_3} \sim MM^{\cdot}$ and the chain transfer to oxygen $\sim M^{\cdot} + O_2 \xrightarrow{k_3} \sim MO_2$ is given by the expression $W_3/W_i = k_3[M]/k_1[O_2] = \alpha$. Using α as a criterion, it is possible to estimate the probability of non-inhibited polymerisation steps in the presence of oxygen. According to estimates, the reaction $\sim M^{\cdot} + M \rightarrow \sim M^{\cdot}$ is suppressed in the temperature range 20–60° C for all vinyl monomers, including vinyl acetate and methyl acrylate which generate the most reactive radicals under the conditions of saturation with oxygen (according to the data in Table 10, the values of α for butadiene, styrene, and methyl methacrylate are 2.8×10^{-3}, 4.4×10^{-3}, and 5×10^{-2} respectively at 50° C).

Thus, during the induction period, the monomer and oxygen react in equimolar proportions via the mechanism represented by the elementary reactions (0), (1), (2), and (6) in Scheme 1; the rate of consumption of oxygen is constant and the reaction is of zero order with respect to O_2. The kinetics of polymerisation inhibited by oxygen[2,26,133] and also by oxygen and antioxidants present simultaneously[134-139] have been examined in detail. The range of oxygen concentrations in which O_2 exerts the maximum inhibiting effect on the polymerisation of monomers is defined by the relation $[O_2] \geqslant k_3[M]/0.1k_1$. Only at the end of the induction period does the O_2 concentration fall to values such that α proves to be greater than 0.1 and the $\sim MO_2^{\cdot} + \sim M^{\cdot}$ chain cross-termination reaction and the $\sim M^{\cdot} + M \rightarrow \sim MM^{\cdot}$ homopolymerisation steps become insignificant.

Since the efficiency of chain transfer to oxygen is extremely high, the $\sim M^{\cdot} + M \rightarrow \sim MM^{\cdot}$ chain propagation steps take place with a very low probability and the only pathway involving the consumption of the monomer becomes the chain regeneration reaction. The kinetic effect of oxygen on the polymerisation of the monomer is therefore determined by the ratio of the rate of chain propagation W_3 in the absence of O_2 to the rate of chain regeneration W_2, where $W_3 = (k_3/k_4^{1/2})[M]W_i^{1/2}$ for $P_{O_2} = 0$ and $W_2 = (k_2/k_6^{1/2}) \cdot [M]W_i^{1/2}$ when peroxy-radicals are responsible for chain termination: $2MO_2^{\cdot} \rightarrow$ chain termination. When the rates of initiation are equal, we obtain $W_3/W_2 = k_3k_6^{1/2}/k_4^{1/2}k_2 \cdot k_3/k_4^{1/2}$ and $k_2/k_6^{1/2}$ vary in opposite senses (Table 10) in the series styrene, acrylonitrile, methyl methacrylate, vinyl acetate, and methyl acrylate, in full agreement with the fact that k_3 is determined by the reactivity of the radical (homopolymerisation) and k_2 is determined by the reactivity of the monomer (oxidative polymerisation). In the above series of compounds the ratio W_3/W_2 increases sharply by three orders of magnitude, the inhibition of polymerisation being more pronounced the less reactive the monomer. This behaviour is a consequence of the decisive role of the reactivity of monomers in oxidative

polymerisation. Increasing inhibition of polymerisation is inevitable when the relatively unreactive peroxy-radicals interact with increasingly less reactive monomers. In homopolymerisation, where the reactivities of the monomers and radicals vary in opposition, the low reactivity of the monomer is swamped by the high reactivity of the radical[32].

Thus the efficiency of the inhibiting effect of oxygen varies in opposition to the reactivity of the monomer in the polymerisation reaction. This behaviour makes it possible to predict the influence of oxygen on radical polymerisation from the available literature values of $k_3/k_4^{1/2}$ and k_3, having adopted styrene as the reference monomer (since $W_3/W_2 \simeq 1$ for this compound in the temperature range 20–70°C).

* * *

It follows from the data presented that the fundamental elementary reactions in the oxidative polymerisation of vinyl monomers have now been established. The mechanism of the oxidative polymerisation of styrene, α-methylstyrene, methyl methacrylate, and butadiene has been studied comparatively fully. The kinetics of the interaction with oxygen of a series of other monomers have also been investigated, but the available information about the rate constants for the elementary reactions remains extremely limited. The results obtained made it possible to determine the nature of the relation between the structure of a vinyl monomer and its reactivity in oxidative polymerisation, and to discover the characteristics of the behaviour of oxygen as an inhibitor of radical-chain polymerisation. In general, oxidative polymerisation, which represents the boundary between radical-chain polymerisation and oxidation, has still been clearly inadequately investigated. A marked deficiency of data on the chemistry, kinetics, and thermodynamics of the interaction of oxygen with unsaturated compounds is felt. The most urgent task is a quantitative investigation of the mechanism of the oxidative polymerisation of vinyl monomers at advanced stages of the reaction, particularly in highly viscous media, including reactions in the solid phase. In combination with the study of macroscopic process kinetics, further studies on these lines will make it possible to lay the theoretical foundations for the formation of films of unsaturated compounds and will permit an expansion of research on the stabilisation of organic protective coatings.

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Dinuclear Iron Carbonyl Complexes with Nitrogen-containing Bridges

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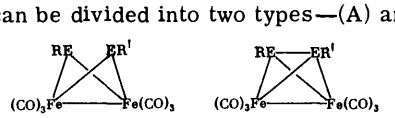
The literature on the synthesis and properties of dinuclear complexes with the $N_2Fe_2(CO)_6$ group is surveyed. It is shown that these complexes are formed in reactions of a wide variety of nitrogen-containing organic compounds with iron carbonyls. The possibility of the formation of nitrene species and their complexes in these reactions is considered. The bibliography includes 123 references

CONTENTS

I.	Introduction	213
II.	Reactions of nitrogen-containing organic compounds with iron carbonyls leading to dinuclear complexes	214
III.	Chemical properties of dinuclear complexes	221
IV.	Results obtained by physical research methods	223

I. INTRODUCTION

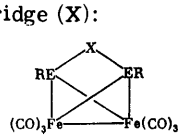
Dinuclear iron carbonyl complexes with heteroatomic bridges are widely known in the chemistry of complex compounds. These compounds include also complexes containing the $Fe_2(CO)_6$ group, in which the iron atoms are linked by an intermetallic bond as well as one six-electron or two three-electron heteroatomic bridges. Depending on the electronic structure of the bridge, these complexes can be divided into two types—(A) and (B):



(A) (B)

Among complexes with three-electron bridges [type (A)], compounds with RS bridges have been known longest (see, for example, Refs. 1–4). Analogous nitrogen-containing compounds were discovered comparatively recently. An example of six-electron bridges is provided by the –S–S–, –NR–NR–, and –PR–PR–† groups. Complexes of type (B) are formed with participation of such bridges.

In their turn three-electron heteroatomic groups can also be linked by a bridge (X):



However, as will be shown below, these compounds differ little in their structural parameters from complexes of type (A).

Interest in transition metal complexes with nitrogen-containing ligands was initially due to the fact that the compounds with the diazene ligand (HN=NH) were regarded as possibly intermediates in the enzymatic fixation of molecular nitrogen[5,6]. However, subsequently

† A.H.Cowley and K.E.Hill, Inorg.Chem., 12, 1446 (1973).

interesting data were obtained fairly rapidly, showing that this field of the chemistry of complex compounds may be of independent importance.

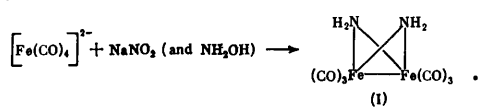
Complexes with nitrogen-containing bridges of types (A) and (B) were obtained by the interaction of various nitrogen compounds with iron carbonyls. During their synthesis, it was found that the formation of complexes of a particular type is controlled by a detailed balance between various factors. Thus it was discovered that the same complex may be generated from a wide variety of types of nitrogen compounds, and, just as surprisingly, compounds of one class, differing from one another merely by the nature of the substituents, can give rise to complexes of different types. This apparent contradiction was resolved on the hypothesis[7] of the intermediate formation in these reactions of either free nitrene species or such species coordinated to the metal. In many cases it was possible to isolate stable nitrene complexes.

Thus the chemistry of these complexes approached very closely that field of coordination chemistry, which has been developing vigorously in recent years, which is concerned with the problems of the stabilisation of unstable organic species as a result of coordination to transition metal complexes[8]. However, it would be incorrect to regard all the reactions of nitrogen compounds with iron carbonyls, leading to dinuclear complexes, as proceeding via the intermediate formation of nitrene species or their complexes. Otherwise the reactions with phenyl azide and azobenzene should have led to the same products, which is not the case. As will be shown below, the electronic and structural factors, the nature of the attacking transition metal complexes, and the reaction conditions determine the chemical behaviour of the nitrogen-containing ligand. It is not at present clear which of these factors predominates, but there is no doubt that the comparatively low strength of the N–N bond, whose dissociation energy is 37 kcal mole^{-1} in certain cases[9] owing to the repulsion of the nitrogen *p* orbitals, does not play the least important role.

In the present review the literature data are classified in terms of the reactions of different organic nitrogen compounds in order to follow more clearly the specific features of the behaviour of each of them. Special reviews devoted to dinuclear iron carbonyl complexes have not yet been published, but these data are considered partially in a number of review articles[8,10–12]. Analogous dinuclear complexes of other transition metals will be briefly mentioned only, for comparison.

II. REACTIONS OF NITROGEN-CONTAINING ORGANIC COMPOUNDS WITH IRON CARBONYLS LEADING TO DINUCLEAR COMPLEXES

The simplest type (A) complex is obtained (in low yield) in the interaction of the anion $[Fe(CO)_4]^{2-}$ with $NaNO_2$ or hydroxylamine under mild conditions[13–16]. It was assumed initially that this compound contains the N–N group. However, its structure was established as that of complex (I) on the basis of mass spectra[17,18] and X-ray diffraction studies[18]:

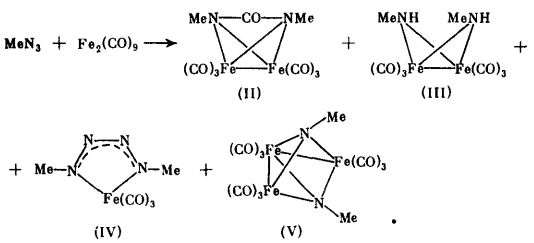


(I)

The reactions of organic nitrogen compounds with iron carbonyls lead as a rule to a mixture of different complexes.

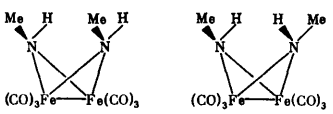
1. Reactions of Azides

Iron carbonyls catalyse the decomposition of organic azides under mild conditions. In most cases these reactions lead to the formation of a mixture of different complexes. The mixture composition varies considerably as a function of the type of organic group in the azide. Thus the reaction of methyl azide with $Fe_2(CO)_9$ gives rise to a mixture of complexes, where the main product is complex (II) with the ligand MeNCONMe‡.[7] The structure of this complex was demonstrated by the diffraction method[19]:



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

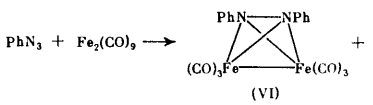
Complex (III) was obtained in a low yield and resolved into the stereoisomeric forms (IIIa) and (IIIb):



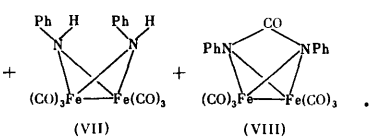
(IIIa) (IIIb)

Complex (IV), with a tetra-azadiene ligand, unknown in a free state, was isolated from the products of this reaction in a high yield (20%). The trinuclear complex (V) is formed in a moderate yield. The yield of the complex in the reaction of $MeNO_3$ with $Fe_2(CO)_9$ [7] is fairly high. Its structure was demonstrated by X-ray diffraction[20].

Phenyl azide reacts just as fast with $Fe_2(CO)_9$, but in this case the main product is the dinuclear complex (VI) with a six-electron ligand containing an N–N bond§[7]. A similar complex was not isolated from the products of the analogous reaction involving methyl azide:



(VI)



(VII) (VIII)

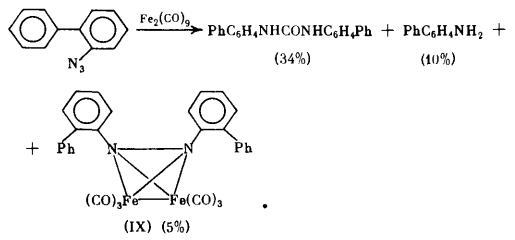
Furthermore, the reaction gives rise to complex (VII) in a low yield. In contrast to the analogous complex (III), obtained by the reaction with methyl azide, complex (VII) was isolated in only one stereoisomeric form. It is unstable in solution and decomposes spontaneously; the diphenylurea derivative (VIII) formed under these conditions was also isolated from the products of the reaction of phenyl azide with $Fe_2(CO)_9$.[7] The same compound is formed when $Fe_3(CO)_{12}$ is used (heating to 90°C).[21]

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‡ It is noteworthy that this product is obtained in a higher yield in the reaction of methyl isocyanate with $Fe_2(CO)_9$.[7]

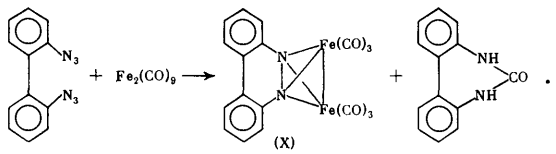
§ Free azobenzene was isolated in this reaction in a negligible yield.

The thermal decomposition of 2-azidobiphenyl is known to result in the formation of carbazole (in a high yield)[22]. However, when this azide decomposes in the presence of $Fe_2(CO)_9$, carbazole is formed in a negligible yield, while the main products of this reaction are *N*,*N*′-bis-(2-biphenylyl)urea (34%), 2-aminobiphenyl (10%), and the dinuclear complex (IX) (5%):[23]



(IX) (5%)

A similar dinuclear complex (X) is formed from a biphenyl derivative containing two azido-groups in the *ortho*-positions in different rings[23]:

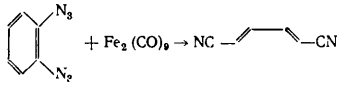


(X)

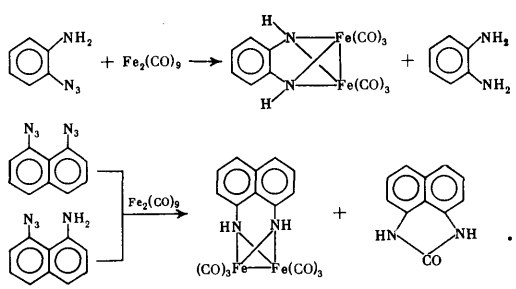
Together with complex (X), a cyclic urea derivative is also formed in this case. The determination of the structure of (X) and its specific synthesis from benzo[*c*]-cinnoline have already been described[24,25].

Thus in the above reactions aromatic azides give rise to dinuclear complexes of type (B) with six-electron nitrogen-containing ligands, while methyl azide gives rise mainly to dinuclear complexes of type (A) with three-electron bridges.

The course of these reactions differs somewhat when two azido-groups or an azido- and an amino-group are present in the *ortho*-positions of the benzene ring or in the *peri*-positions in the naphthalene molecule. Only *cis*,*cis*-muconitrile was isolated from the products of the reaction of *o*-diazidobenzene (27%):[23]



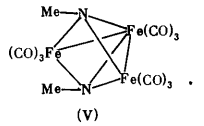
Under the same conditions, *o*-azidoaniline, 1,8-diazidonaphthalene, and 1-amino-8-azidonaphthalene form, together with purely organic products, dinuclear complexes in which the nitrogen atoms are linked by *o*-phenylene or *peri*-naphthalene bridges[23]:



These results show that steric factors can also play a significant role in the formation of products.

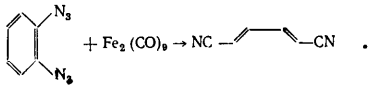
The hypothesis of the formation of nitrene species in the decomposition of azides in the presence of transition metal compounds does not lack justification, since in many cases complexes with such species have been isolated.

It has been shown by X-ray diffraction[19] that the trinuclear cluster (V), isolated from the products of the reaction of methyl azide with $Fe_2(CO)_9$,[7] is a complex in which each nitrene species $CH_3\dot{N}$: is coordinated to three iron atoms:



(V)

The iron complex (XI) of $Me_3Si\dot{N}$: was isolated from the products of the reaction of trimethylsilyl azide with $Fe_2(CO)_9$. This complex proved to be a trinuclear cluster incorporating a triply coordinated trimethylsilylnitrene species. It is of interest that one of the carbonyl groups in this cluster is also linked to three iron atoms[26,27]:



Stable nitrene complexes have also been obtained by the reaction of a polyfluorinated azide with ruthenium and osmium carbonyls[28]¶:

$$Ru_3(CO)_{12} + CF_3CHFCF_2N_3 \rightarrow Ru_3(CO)_9(NCF_2CHFCF_3)_2;$$
$$M(CO)_3(PPh_3)_2 + CF_3CHFCF_2N_3 \rightarrow M(NCF_2CHFCF_3)(CO)_2(PPh_3)_2;$$
$$M = Ru, \text{ or } Os.$$

Azides with other electron-accepting organic groups gave isocyanate complexes on interaction with the same ruthenium compound[29]:

$$RN_3 + Ru(CO)_3(PPh_3)_2 \rightarrow Ru(CO)_2(PPh_3)_2(RNCO);$$
$$R = PhCO,\ p\text{-}MeC_6H_4CO,\text{ or } p\text{-}MeC_6H_4SO_2.$$

In the presence of proton donors these complexes decompose with formation of isocyanate derivatives. It is of interest that the reaction of benzoyl azide or β-benzoylvinyl azide with $Fe_2(CO)_9$, carried out in aqueous alcohol, also led to derivatives of the corresponding isocyanates[30]:

$$RN_3 + Fe_2(CO)_9 \rightarrow [(RNCO)Fe(CO)_4] \xrightarrow[\text{alcohol, water}]{} [RN{=}C{=}O] \rightarrow RNHCOOC_2H_5 + RNH_2;$$
$$R = C_6H_5CO \text{ or } C_6H_5COCH{=}CH$$

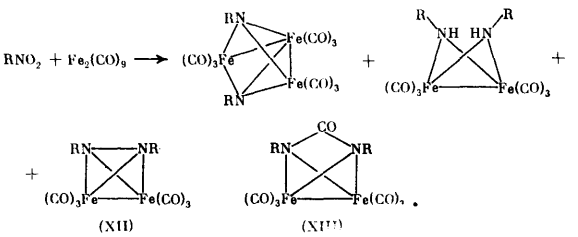
Speaking of the formation of isocyanates, one should bear in mind that, in the absence of transition metal complexes, nitrenes combine with carbon monoxide under very severe conditions[31-34].

The interaction of 1-azidostyrene with $Fe_2(CO)_9$ [35] is examined below in the section dealing with the reactions of azirines.

¶ See the review of Genini and La Monica[8] for information about other stable nitrene complexes of transition metals obtained from azides.

2. Reactions of Nitro-compounds

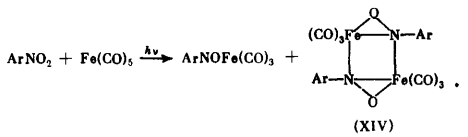
The reaction of nitromethane with $Fe_2(CO)_9$ gives the same mixture of products as the reaction with methyl azide [7]. Other aliphatic nitro-compounds, such as 1-nitro- and 2-methyl-2-nitropropanes, give rise to complexes (XII) with an N–N bond in addition to all the above products [36]. The main product of the reaction of 1-nitropropane with $Fe_2(CO)_9$ is, as for nitromethane, a trinuclear nitrene complex, while the reaction involving 2-methyl-2-nitropropane gives compound (XIII) in the highest yield:



(XII) (XIII).

Heating of aliphatic nitro-compounds with $Fe(CO)_5$ in diglyme at 120–132°C leads only to organic products—derivatives of formamide and urea [36]. The same products have been obtained on thermal degradation (120–130°C, diglyme) of certain iron carbonyl complexes isolated from the products of reactions with nitro-compounds. This suggested that iron carbonyl complexes may be intermediates in the formation of formamide and urea derivatives [36].

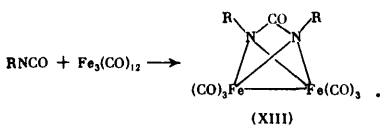
It is of interest that, on reaction with $Fe(CO)_5$ under ultraviolet or γ-irradiation, nitrobenzene forms nitrosobenzene complexes [37,38]. The structure of the dinuclear complex (XIV) was determined by X-ray diffraction [39]:



(XIV)

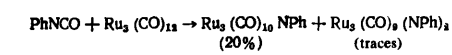
3. Reactions of Isocyanates

A report of the formation of an isocyanate complex on reaction of isocyanates RNCO (R = Me, n-Bu, or Ph) with $Fe_3(CO)_{12}$ was published in 1964. [21] Later studies established the presence of the ureylene group in these compounds and structure (XIII) was attributed to them [7,40], which was confirmed by X-ray diffraction [41]:



(XIII)

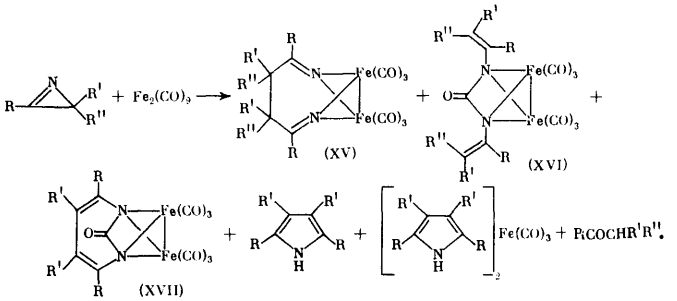
Intermediate complexes containing an isocyanate ligand can probably be formed in reactions with isocyanates. As shown above, such complexes were isolated in some cases [8]. At the same time it is important to note that nitrene complexes can also be obtained from isocyanates: this was observed in the reaction of phenyl isocyanate with $Ru_3(CO)_{12}$: [42]



4. Reactions of Azirines

The reactions of azirines with $Fe_2(CO)_9$ have been investigated in detail [35,43]. When these compounds are heated at 50°C (3–4 h) in dry benzene, the dinuclear complexes (XV), (XVI), and (XVII), which are stable in air, and certain organic substances are formed:

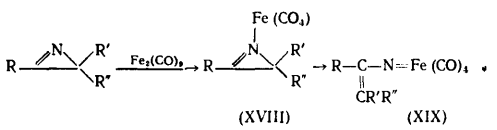
Scheme 1



a) R = Ph, R′ = R″ = H; b) R = *p*-$CH_3C_6H_4$, R′ = R″ = H; c) R = *p*-BrC_6H_4, R′ = R″ = H; d) R = Ph, R′ = Me, and R″ = H; e) R = Ph, R′ = C_2H_5, R″ = H; f) R = CH_3, R′ = $CH(Me)_2$, R″ = H; g) R = Ph, R′ = R″ = Me.

The structure of the products isolated was confirmed by spectroscopic data. It has been suggested [35] that a complex of type (XVIII) is involved in this reaction and is subsequently converted, with ring opening, into the nitrene derivative (XIX), which is the parent compound of all the products formed.

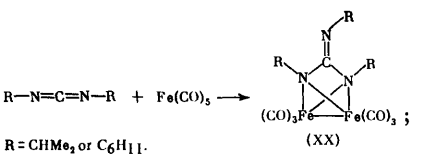
It is important to note that, on reacting with $Fe_2(CO)_9$, 1-azidostyrene gives rise to virtually the same products as phenylazirine, with the exception of pyrrole and its complex, which confirms the importance of the formation of the intermediate nitrene species (free or in the form of a metal carbonyl complex) [35]:



(XVIII) (XIX)

5. Reactions of Carbodi-imides

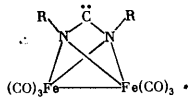
The reactions of carbodi-imides with $Fe(CO)_5$ give rise to dinuclear complexes (XX), whose acid hydrolysis indicates the presence in their molecules of the trialkylguanidine species linked to the $Fe_2(CO)_6$ group (see Section III). The infrared, NMR, and mass spectrometric data agree with formula (XX):



R = $CHMe_2$ or C_6H_{11}. (XX)

In the course of the discussion of the possible mechanism of the formation of this complex, a scheme involving the intermediate formation of the carbene species (XXI) was put forward. This species reacts further with a second carbodi-imide molecule and forms the complex (XX) and an isonitrile, isolated in the form of the compound

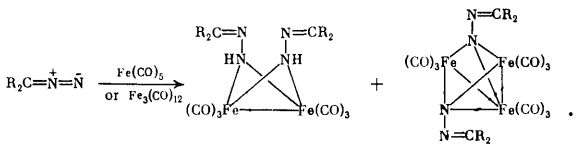
$(C_6H_{11}NC)Fe(CO)_4$:



(XXI)

6. Reactions of Diazo-compounds

Two types of complexes were isolated from the products of the reactions of diphenyl- and di-(*p*-tolyl)-diazomethanes with $Fe(CO)_5$ or $Fe_3(CO)_{12}$: an orange dinuclear complex (XXII) and a black trinuclear complex (XXIII).[44] The structures of the two complexes were confirmed by X-ray diffraction[44,45]:



(XXII) (XXIII)

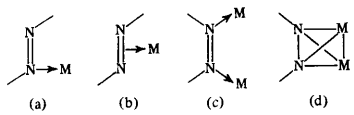
7. Reactions of Azo-compounds

Up to 1963, there was almost no information in the literature about the reactions of transition metal derivatives with azo-compounds, except for the description of certain metal chelate complexes of azo-dyes. However, from 1963, after the publication of the study of Kleiman and Dubeck[46] on the reactions of azobenzene with nickelocene, a series of other publications appeared in which complexes of azobenzene and its derivatives with platinum(II), palladium(II), and zerovalent iron were described[47-49].

Different ways of coordinating the N=N bond to transition metals (see Scheme 2) attracted the attention of chemists[10,11,24,50-54]. Of the four possible types of structures (a–d) of iron carbonyl complexes with azo-compounds, three structures were detected (a, c, and d), in which the nitrogen-containing ligand behaves as a donor of two, four, and six electrons respectively.

The type of coordination (b) is encountered in complexes of other transition metals, for example, $NiL_2(PhN{=}NPh)$[55-62] and $(C_5H_5)_2M(PhN{=}NPh)$ (M = Ti or V),[63] i.e. in those cases where the azo-compound is a comparatively poor σ-donor and the metal-containing fragment is a poor σ-acceptor.

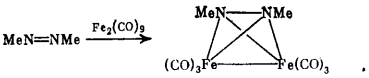
Scheme 2



(a) (b) (c) (d)

Azo-compounds with a wide variety of structures have been made to react with iron carbonyls. Studies have shown that the behaviour of aliphatic azo-compounds differs appreciably from that of azobenzene and its substituted derivatives.

The interaction of azomethane with di-iron nonacarbonyl leads to a dinuclear hexacarbonyl complex in which the initial compound retains its skeleton[64]. The ligand behaves in this case as a six-electron donor. The structure of the complex was demonstrated by X-ray diffraction:



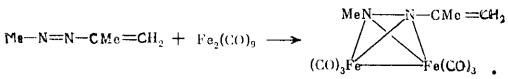
It is noteworthy that the dissociation of the bond between the nitrogen atoms has been observed for hexafluoroazomethane, which gives rise to a mixture of *cis*- and *trans*-isomers of the nitrene complexes $(Ph_2PMe)_2Ir.(CO)(Cl)(NCF_3)$ on treatment with *trans*-$ClIr(CO)(Ph_2.PMe)_2$:[65]

$(Ph_2PMe)_2Ir(CO)(Cl)(NCF_3)$[65]:

$$CF_3N{=}NCF_3 + \textit{trans}\text{-}ClIr(CO)(Ph_2PMe)_2 \rightarrow \textit{cis}\text{- and } \textit{trans}\text{-}(Ph_2PMe)_2Ir(CO)Cl(NCF_3).$$

Unfortunately the reactions of iron carbonyls with hexafluoroazomethane have not been investigated.

The reaction of di-iron nonacarbonyl with 2-(methylazo)propane is very remarkable[66]. In contrast to other butadiene systems, this compound gives rise to a dinuclear complex to which structure (XXIV) was attributed on the basis of spectroscopic data. The vicinal disposition of the nitrogen atoms in this compound has a decisive influence on the structure of the complex, while the C=C double bond is not involved in coordination[66]:

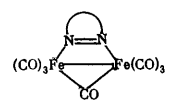


(XXIV)

This is not surprising if one takes into account the quantum-chemical calculations on the PhCH=CHPh and PhN=NPh molecules[67,68], where the energies of the highest occupied molecular orbitals (HOMO) are approximately equal, while the lowest unoccupied molecular orbital (LUMO), which is in both cases π^*-antibonding, lies in a far lower position for azobenzene†.

Cyclic azo-compounds also retain their skeleton in reactions with iron carbonyls. Dinuclear iron carbonyl complexes of type (B) have been obtained from 2,3-diazabicyclo[2,2,1]hept-2-ene,[51-53] derivatives of 1,2-diazacyclopent-1-ene,[50,69,70] 1,3,4-thiadiazoline,[53] and dibenzo[1,4,5]oxadiazepine.[24,25]. It is noteworthy that in these reactions the first stage involves the formation of the mononuclear complexes $LFe(CO)_4$,[50,53] in which the metal atom is coordinated to one of the nitrogen atoms[70] and the ligand occupies an axial position.

Together with these compounds, complexes of the type $LFe_2(CO)_7$ were isolated in the reactions involving 2,3-diazabicyclo[2,2,1]hept-2-ene and 1,3,4-thiadiazoline[53]. On the basis of infrared and ^1H NMR spectra, the following structure was attributed to these complexes:

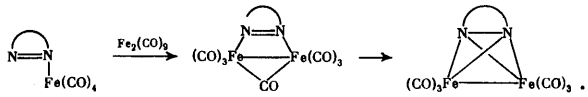


(XXV)

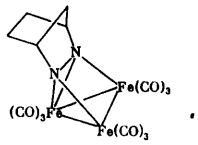
The infrared spectra of these compounds exhibit absorption by the metal carbonyl bridge groups in the range 1770–1820 cm^{-1}.[53] Compounds of type $LFe(CO)_4$ and $LFe_2(CO)_7$ are apparently intermediates[51,53] in the

† For information about the electronic structures of compounds with the –N=N– group, see, for example, Albini and Kisch's review[12].

formation of the dinuclear complexes $LFe_2(CO)_6$, since the conversion of $LFe(CO)_4$ into $LFe_2(CO)_7$ and then into $LFe_2(CO)_6$ can be followed by infrared spectroscopy in the region of approximately 2000 cm^{-1}.



It has been shown recently that a complex of type $LFe(CO)_4$, where L = diazanorbornene, reacts with iron carbonyls and can give rise to the trinuclear cluster (XXVI) together with a dinuclear complex of type $LFe_2(CO)_6$ and the former can also be synthesised by irradiating a dinuclear type (A) complex ($\lambda \geqslant 300$ nm) in the presence of iron carbonyls[51]:

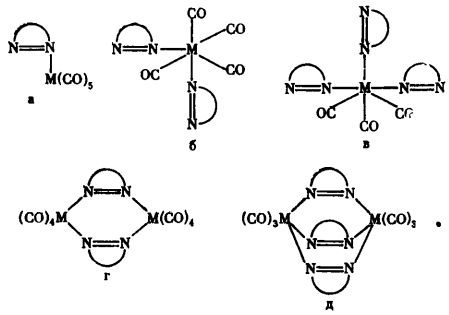


(XXVI)

Bearing in mind that the dinuclear complexes are diamagnetic, it follows that, in conformity with the effective atomic number rule, the metal atoms in them should be linked by an intermetallic bond, whose presence has been confirmed by X-ray diffraction (see below).

It is of interest that Group VIB metal carbonyls react with azo-compounds to give, together with mononuclear complexes (of types a–c, Scheme 3), also dinuclear complexes of types d and e in which the ligand behaves as a four-electron donor and the metal atoms are not linked to one another[6,71–75]:

Scheme 3



Thus Group VIB metals form a bond with nitrogen atoms solely via lone electron pairs, while the π electrons of the N=N group are not involved in bonding to the metal, in contrast to iron carbonyl complexes. This can probably be attributed to the fact that the lowest unoccupied antibonding orbital of azo-compounds is located sufficiently low to make possible their interaction with Group VIB metals.

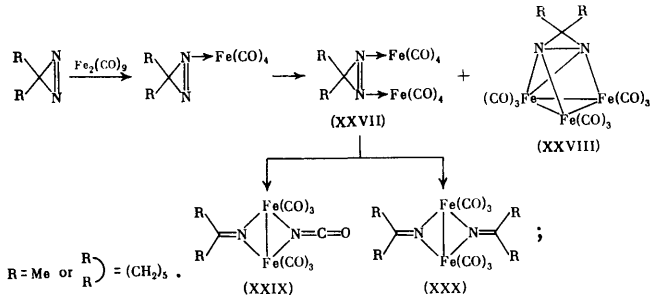
We may note that, instead of a mixed complex of type d, the reaction of $L_2Mo(CO)_4$ (where L = diazanorbornene) with $Fe_2(CO)_9$ gave a dinuclear di-iron hexacarbonyl complex of type $LFe_2(CO)_6$.

The reaction with diazirines, which are strained cyclic azo-compounds, is a special case. Diazirines contain the N=N group in a three-membered ring, and the distribution of electron density in these compounds differs significantly from that in other cyclic azo-compounds.

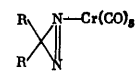
MINDO/2 calculation for 3,3-dimethyldiazirine[76] led to the conclusion that the orbitals of the C–N σ bond are appreciably mixed with a linear combination of those of free pairs of n_- and n_+ electrons of the nitrogen atoms, so that the concept of a "free pair" apparently loses its significance in these compounds. Calculation showed that the electrons are localised on the nitrogen atoms to an extent of only 56%,[76] so that the possibility of the formation of complexes of diazirines with metals appears to be problematical.

However, in reality it was found that[54] 3,3-dimethyl- and 3,3-pentamethylene-diazirines in tetrahydrofuran (THF) react with $Fe_2(CO)_9$ to form unstable complexes of the type $LFe(CO)_4$ (Scheme 4), which are subsequently converted into compounds (XXVII), giving rise also to a small amount of the trinuclear cluster (XXVIII). The diazirine skeleton is retained in all these compounds. Complexes (XXVII) decompose in solution with formation of new, more stable compounds (XXIX) and (XXX), which can be synthesised directly from diazirines and $Fe_2(CO)_9$ or $Fe(CO)_5$ on irradiation. This entails the dissociation of the C–N and N=N bonds and it is postulated that intermediate nitrene species are formed in the latter case[54]:

Scheme 4



Analogous results have been obtained in a study[77] in which the structure of complex (XXX) [where R–R = $(CH_2)_5$] was confirmed by X-ray diffraction. It is of interest that the aquopentammineruthenium derivative $[Ru(NH_3)_5(H_2O)]^{2+}$ used in the above study in the reaction with 3,3-pentamethylenediazirine promotes only the dissociation of the C–N bonds, which results in the formation of a complex with molecular nitrogen, namely $[Ru(NH_3)_5N_2]^{2+}$,[77] while in the reaction with $Cr(CO)_6$ the diazirine skeleton is retained and only complex (XXXI) is formed[54]:



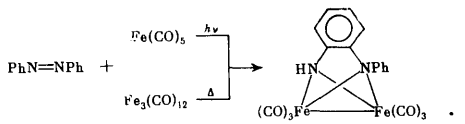
(XXXI)

The above examples provide a good illustration of the major influence of the metal in the attacking complex on the behaviour of the azo-compound.

The cleavage of the N=N bond is a new phenomenon in the chemistry of diazirines. However, a similar phenomenon is fairly usual in reactions of aromatic azo-compounds with iron carbonyls. At the same time it is important to note that the behaviour of such azo-compounds depends in many respects, as will be shown below, on the nature of the substituent in the aromatic ring.

The interaction of azobenzenes with $Fe_2(CO)_9$ was investigated for the first time by Bagga et al.[49] X-Ray diffraction analysis established[78,79] that the complex isolated has the structure (XXXII), indicating the dissociation

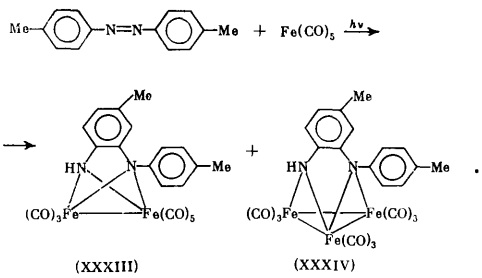
of the N=N bond as a result of an orthosemidine rearrangement‡:



(XXXII)

The yields of compound (XXXII) are only 2–3% both in the photochemical reaction of azobenzene with $Fe(CO)_5$ and in the thermal reaction with $Fe_3(CO)_{12}$.[80] At the same time in one of the reports[24] it is stated briefly that the reaction of azobenzene with $Fe_2(CO)_9$ at room temperature results in the formation of an unstable complex in which the azobenzene ligand is probably incorporated without serious changes, since azobenzene is liberated in attempts to purify the complex chromatographically or by sublimation. It is of interest that, as already stated above, a comparatively stable complex of type (B) with the azobenzene ligand is formed in the reaction of phenyl azide with $Fe_2(CO)_9$.[7]

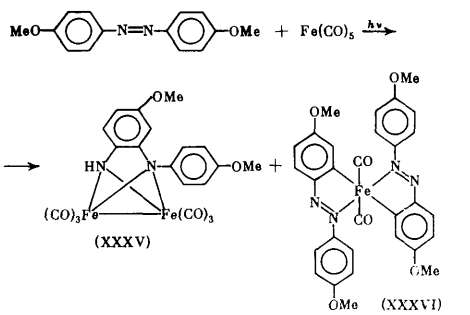
The behaviour of ring-substituted azobenzenes in reactions with iron carbonyls differs from the behaviour of azobenzene itself. Thus, when 4,4′-dimethylazobenzene reacts with $Fe(CO)_5$ under irradiation, two complexes with the *ortho*-semidine ligand are formed: a dinuclear complex (XXIII) in 2% yield and a trinuclear complex (XXXIV), which becomes the sole product when $Fe_2(CO)_9$ is used instead of $Fe(CO)_5$:[80]



(XXXIII) (XXXIV)

The structures of these complexes were assigned on the basis of spectroscopic studies and data derived from chemical reactions[80].

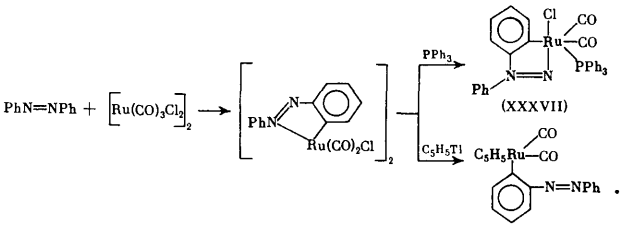
Under the same conditions, 4,4′-dimethoxyazobenzene gives a 22% yield of complex (XXXV) and a small amount of a completely new compound (XXXVI), which is a product of ring metallation[80]:



(XXXV) (XXXVI)

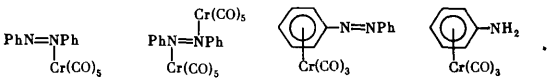
‡ When complexes of the type η^5-$C_5H_5M(CO)_2$, where M = Co (I) or Rh (I), are used in the reaction of azobenzene, dinuclear complexes with the *ortho*-semidine skeleton are also formed[81].

It is important to note that ring-metallated chelate complexes of type (XXXVI) are obtained fairly frequently when other metal carbonyls are used in the reaction with azobenzene[82–87]. Thus $[Ru(CO)_3Cl_2]_2$ yields a dimer, which is converted into complexes (XXXVII) and (XXXVIII) respectively on treatment with Ph_3P and C_5H_5Tl:[84]

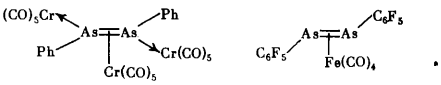


(XXXVIII)

Depending on the conditions, chromium hexacarbonyl yields at the same time four complexes[88]:



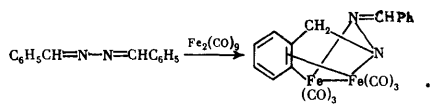
It is noteworthy that azobenzene does not react with metal carbonyls to form π complexes via the N=N bond, while its arsenic analogue yielded the π complexes (XXXIX) and (XL):[89,90]



(XXXIX) (XL)

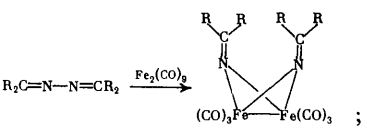
8. Reactions of Azines

There is at present no clear-cut hypothesis concerning the electronic and structural factors responsible for the different types of behaviour of azines in reactions with iron carbonyls. Thus the bond between the nitrogen atoms is retained in benzylideneazine on reaction with $Fe_2(CO)_9$ and a complex is formed to which the following structure was attributed on the basis of spectroscopic data[49]:



(XLI)

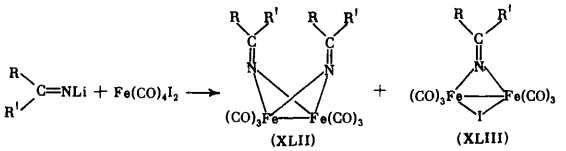
Benzophenone azine and its 4,4′-dimethyl derivative react with iron carbonyls to give low yields of di-iron hexacarbonyl complexes of type (XLII) whose formation involves the dissociation of the N–N bond[49]. The structure of these complexes has been demonstrated by X-ray diffraction in relation to compound (XLIIb):



(XLII): a) R = Ph; b) R = *p*-MeC_6H_4.

After unsuccessful attempts to improve this method of synthesis, a different procedure was proposed, which also leads to the formation of a small amount of compound

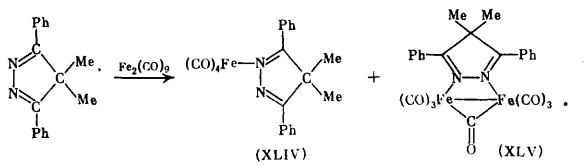
(XLIII):[92]



(XLII) (XLIII)

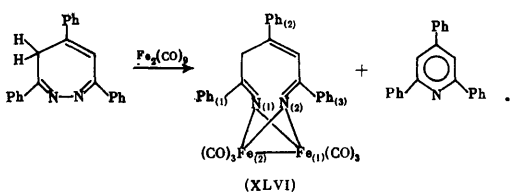
(a) R = R' = Ph; (b) R = R' = *n*-MeC$_6$H$_4$; (c) R = Ph, R' = t-Bu.

The unstrained cyclic azine 5,5-dimethyl-1,4-diphenyldiazacyclopentadiene reacts with $Fe_2(CO)_9$ under mild conditions (25°C) in pentane to form two complexes: a mononuclear complex (XLIV) and a dinuclear complex (XLV):[93]



(XLIV) (XLV)

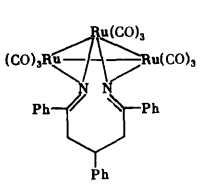
In agreement with infrared spectroscopic data, complex (XLV) incorporates a CO bridge group [ν(CO) = 1736 cm^{-1}]. The nitrogen-containing ligand plays in this case the role of a four-electron donor. A cyclic seven-membered azine, such as 3,5,7-triphenyl-4*H*,1,2-diazepine, gives rise in this reaction to the dinuclear complex (XLVI) with dissociation of the N–N bond[94–96]:



(XLVI)

In the study of the Mössbauer spectra of this complex[94] the iron atoms were found to be non-equivalent, which was explained, after X-ray diffraction study, by differences between the Fe–N [$(Fe_1-N)_{av}$ and $(Fe_2-N)_{av}$] bond lengths (1.920 and 1.965 Å respectively). The differences between the bond lengths can be caused in their turn by the steric effects of the two phenyl substituents in the ring, namely $Ph_{(1)}$ and $Ph_{(3)}$, located on the same side of the ring as $Fe_{(2)}$.

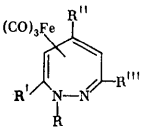
An analogous complex has been obtained as a result of the reaction of 3,5,7-triphenyl-4,5,6-trihydro-1,2-diazepine with $Fe_2(CO)_9$.[84] It is of interest that the use of $Ru_3(CO)_{12}$ in this same reaction led to the trinuclear cluster (XLVII):[94]



(XLVII)

At the same time the reactions of $[Rh(CO)_2X]_2$ (where X = Cl or Br) with seven-membered heterocycles give rise to complexes of type $LRh(CO)_2X$ in which the metal is coordinated to one of the nitrogen atoms[94]; this was confirmed by X-ray diffraction analysis of the compound with the 3,5,7-triphenyl-4*H*-1,2-diazepine ligand (X = Cl).[96]

As in the series of *N*-substituted 1(1*H*),2-diazepines, the breakdown of the diazepine system leads to mononuclear complexes of type (XLVIII) with coordination between the metal atom and the diene group in the heterocycle[97–99]:

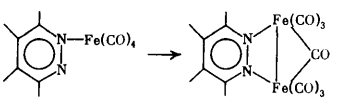


(XLVIII)

9. Reactions of Aromatic Heterocycles with Two Vicinal Nitrogen Atoms

Since the resonance hybrid of aromatic heterocycles incorporates structures with both N=N and =N–N= groups, it is not surprising that iron carbonyls react with these heterocycles in the same way as with azo-compounds and diazines.

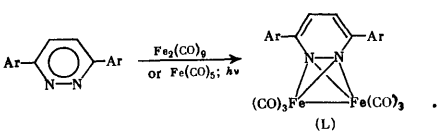
The simplest representative of this class of compounds, namely pyridazine, and also 3,6-dimethylpyridazine react with $Fe_2(CO)_9$ to form in the first stage mononuclear complexes of type $LFe(CO)_4$ in which the metal atom is bound to one of the nitrogen atoms[53,100]. Next, according to Herberhold and Leonard[53], complexes of type $LFe(CO)_4$, formed from pyridazine and phthalazine, are converted into dinuclear compounds (XLIX). In these compounds the ligand behaves as a four-electron donor coordinated to the $Fe_2(CO)_7$ group and containing the CO bridge group in the pyridazine complex [$\nu(CO)_{bridge}$ = 1851 cm^{-1} in KBr and 1775 cm^{-1} in THF solution]. The presence of seven carbonyl groups in the complexes (XLIX) has been confirmed convincingly by mass spectrometry[53]:



(XLIX)

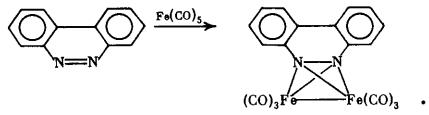
It is noteworthy that the attempt to convert compounds of type $LFe_2(CO)_7$ into $LFe_2(CO)_6$, which was achieved for dinuclear iron carbonyl complexes of aliphatic azo-compounds, was unsuccessful[53]. On heating or irradiation in the presence of CO the complex (pyridazine)$Fe_2(CO)_7$ regenerates (pyridazine)$Fe(CO)_4$.[53]

The reaction of 3,6-diarylpyridazine with $Fe_2(CC)_9$ gives rise to iron carbonyl complexes (L)[123] Their structure was demonstrated by X-ray diffraction analysis of the monotriphenylphosphine derivative[101]:



(L)

An analogous dinuclear complex (LI) was obtained (in 79% yield) from benzo[*c*]cinnoline [24] §:



(LI)

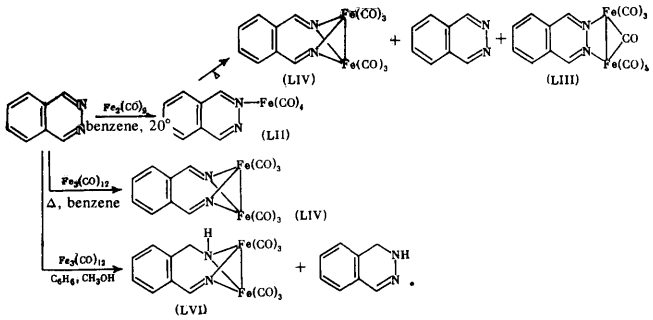
Its structure was also confirmed by X-ray diffraction [25]. In the reaction involving benzo[*c*]cinnoline the formation of an intermediate di-iron heptacarbonyl complex with a CO bridge group was noted [53]. Thermal or photochemical decarbonylation of $LFe_2(CO)_7$ (L = benzocinnoline) leads to complex (LI). The synthesis of dinuclear complexes from 1,10-dichloro- and 3,8-dichloro-benzo[*c*]cinnolines and from 4,5,9,10-tetra-azapyrene has also been mentioned [24], both N=N fragments in the last compound being coordinated to $Fe_2(CO)_6$ groups.

The above examples suggest that the formation of the $N_2Fe_2(CO)_6$ group is energetically fairly favourable, since it occurs despite the losses of resonance energy as a result of the breakdown of the aromatic system of the heterocycle.

Phthalazine forms mononuclear and dinuclear complexes with iron carbonyls (Scheme 5). When it is treated with $Fe_2(CO)_9$ in n-hexane or benzene at 20°C, a mononuclear complex of type $LFe(CO)_4$ (LII) is formed, in which the nitrogen-containing ligand occupies an axial position. Furthermore, a dinuclear heptacarbonyl complex $LFe_2(CO)_7$ (LIII) with a CO bridge group is formed [ν(C=O) = 1745 cm^{-1} in KBr or 1775 cm^{-1} in THF]. [53,104]

According to Alper's data [104], on heating in benzene complex (LII) is converted into a compound $LFe_2(CO)_6$, to which structure (LIV) was assigned. In contrast to di-iron hexacarbonyl complexes of 3,6-diarylpyridazine, there is no bond between the nitrogen atom in compound (LIV). The latter is formed also when phthalazine is heated with $Fe_3(CO)_{12}$ in benzene [104]. The alternative *ortho*-xylylene structure (LV) for this substance has been rejected on the grounds that the ligand in (LIV) retains its benzenoid structure.

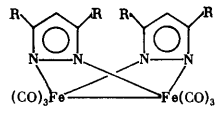
Scheme 5



A dinuclear complex (LVI) (Scheme 5) was detected in the products of the interaction of phthalazine with $Fe_3(CO)_{12}$ in benzene in the presence of methanol [104].

§ It is noteworthy that the reaction of benzo[*c*]cinnoline with Group VIB metal hexacarbonyls gives rise to complexes $LM(CO)_5$, in which the metal is coordinated to one of the nitrogen atoms [102,103].

The reactions of five-membered heterocycles have so far been little investigated. It has been shown that, when pyrazole or 3,5-dimethylpyrazole reacts with $Fe_2(CO)_9$ in ether, dinuclear hexacarbonyl complexes of type (LVII), whose structure has been assigned on the basis of spectroscopic data, are formed together with other products [105,106]:



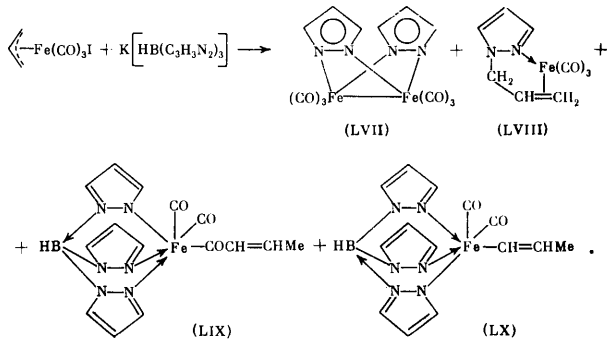
(LVII) ;

R = H, or Me.

The same dinuclear complex (LVII) (R = H) has been obtained by the interaction of $Fe(CO)_4I_2$ with pyrazolylsodium [106]:

$$2Fe(CO)_4I_2 + 2C_3H_3N_2Na \rightarrow (C_3H_3N_2)_2Fe_2(CO)_6 + 2NaI + 2CO$$

and has also been isolated from the products of the reaction of π-(allyl)$Fe(CO)_3I$ with $K[HB(C_3H_3N_2]_3$. [107] The mononuclear complexes (LVIII)–(LX) were obtained together with this product in the latter case:



(LVII) (LVIII)

(LIX) (LX)

III. CHEMICAL PROPERTIES OF DINUCLEAR COMPLEXES

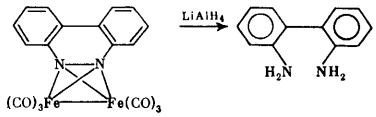
The reactivity of the dinuclear complexes has still been little investigated. Studies have been made mainly on reactions designed to demonstrate the structures of these compounds and, particularly, in order to elucidate the nature of the nitrogen-containing ligand incorporated in them. Thus, *N*,*N*',*N*''-tricyclohexaguanidine, identified as the picrate, was isolated after the acid hydrolysis of complexes of type (XX) (R = C_6H_{11}): [108]

$$(XX) \xrightarrow{H^+} C_6H_{11}NHCNHC_6H_{11} \quad (\text{with } NC_6H_{11})$$

N,*N*'-Diphenylurea was obtained in 50% yield by treating complex (VIII) with $LiAlH_4$, which confirms the presence of this ligand in the complex [41]:

$$(VIII) \xrightarrow{LiAlH_4} PhNHCONHPh$$

On interaction with $LiAlH_4$, the dinuclear benzo[*c*]cinnoline complex forms 2,2-diaminobiphenyl in 56% yield [24]:



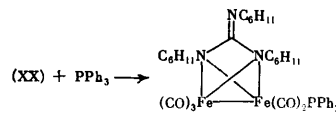
Under the same conditions, free benzo[*c*]cinnoline is resistant to the action of $LiAlH_4$, but, when the complex

is treated with an oxidant, such as Ce^{4+}, free benzo[*c*]-cinnoline may be produced.

The CO ligand substitution reactions involving these complexes are also striking. It has been shown in many instances that phosphines, phosphites, arsines, and isonitriles substitute one and in some cases two CO groups without change in the main skeleton of the complex.

Triphenylphosphine substitutes one or two CO groups in the complex $[Fe_2(CO)_6(NH_2)_2]$ giving rise to compounds of type $[Fe_2(CO)_5PPh_3(NH_2)_2]$ and $[Fe_2(CO)_4(PPh_3)_2(NH_2)_2]$.[17,109] It is of interest that the latter can be very readily oxidised by iodine with formation of the dication $[Fe_2(CO)_4.(PPh_3)_2(NH_2)_2]^{2+}$.[17] It is also noteworthy that NO completely displaces the CO ligands from the complex $[Fe_2(CO)_6(NH_2)_2]$.[14,15]

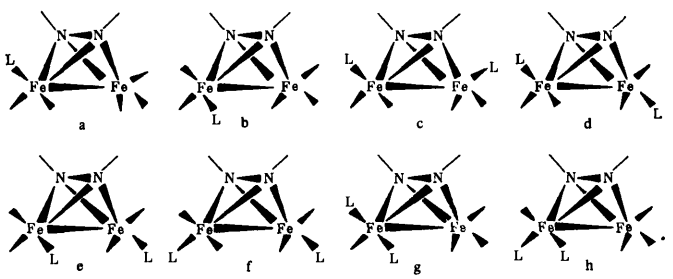
Only one CO group is substituted in a complex of type (XX) (R = C_6H_{11}) by PPh_3 even in the presence of an excess of the latter; this reaction results in the formation of a monophosphine derivative, which is very stable in air[108]:



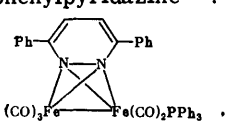
When the di-iron hexacarbonyl complex of benzo[*c*]cinnoline is treated with phosphines, phosphites, arsines, and isonitriles, both mono- and di-substituted derivatives are formed[24,110]. Here it is significant that the substitution of one of the CO groups by another ligand should theoretically lead to two isomers [(a) and (b) (Scheme 6)], while substitution of two CO groups should lead to six isomers [(c)–(h) (Scheme 6)].

Analysis of the infrared spectra of monosubstituted benzo[*c*]cinnoline complexes suggested that these compounds have the structure of the *trans*-isomers (a):[110]

Scheme 6



trans-Substitution¶ relative to the Fe–Fe bond has been demonstrated by the X-ray diffraction study of the triphenylphosphine complex (LXI) obtained from di-iron hexacarbonyl-3,6-diphenylpyridazine[101]:

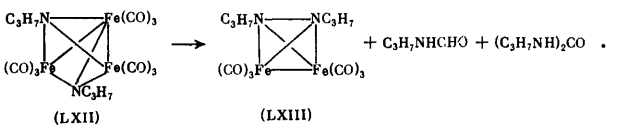


(LXI)

The problem of the structure of the disubstituted derivatives has still not been finally solved. Isomers of types (g) and (h) (Scheme 6) were ruled out on the grounds that the mass spectra of the diphosphite and di-isonitrile complexes investigated, obtained from di-iron hexacarbonyl–benzo[*c*]cinnoline, failed to reveal fragment ions containing one iron atom linked to two $P(OCH_3)_3$ or $C_6H_{11}NC$ molecules[110]. It is extremely difficult to choose between isomers (c)–(f) (Scheme 6). On the basis of the number of bands in the metal carbonyl part of the spectrum, it was concluded that a mixture of isomers is formed in most instances, but it could not be resolved chromatographically[110].

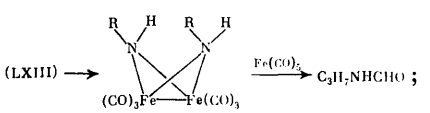
Extremely useful information about the reactivity of dinuclear iron carbonyl complexes was obtained in a study of the interconversions and thermal degradation of these compounds. The study of the products of the reactions makes it possible to some extent to infer the sequence of stages in the formation of dinuclear complexes.

It has been shown[36] that, when the trinuclear complex (LXII) is heated in diglyme at 120–130°C, complex (LXIII) and traces of C_3H_7NHCHO and $(C_3H_7NH)_2CO$ are formed:



(LXII) (LXIII)

On further heating, complex (LXIII) is converted into (LXIV) with rupture of the N–N bond in the bridge ligand:



(LXIV) R = C_3H_7.

When this compound is heated with iron pentacarbonyl, a formamide derivative is formed. Thermal degradation of complex (XIII) (R = C_3H_7) with a ureylene ligand led to the formation of *N*,*N*′-disubstituted urea and the formation of a small amount of complex (XII):

$$(XIII) \xrightarrow[\text{diglyme}]{} (XII) + (RNH)_2CO .$$

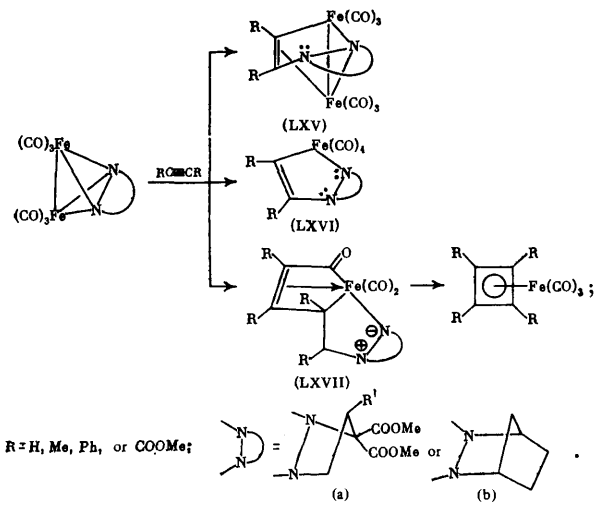
One should note here that the nature of the substituent R can influence the course of the reaction. Thus spontaneous reconversion of complex (XII) into (XIII) for R = Ph has been observed[7]. Prolonged heating of a type (XIII) complex (R = t-Bu) yields substituted formamide and urea[36].

Thus trinuclear complexes of type (LXII) can behave as precursors of binary compounds when the latter are formed from azides and nitro-compounds. Reactions involving insertion in the N–Fe bond can be assigned to the most interesting and hitherto little investigated branch of the chemistry of dinuclear complexes. The insertion of CO molecules in this bond has already been mentioned. Thermal and photochemical reactions of dinuclear complexes with alkynes were investigated recently[111–113] and it was found that alkyne molecules are inserted in the N–Fe bond with formation of complex (LXV)–(LXVII)

¶ We have in mind the *trans*-substitution relative to the Fe–Fe bond in the distorted octahedron at each Fe atom.

Scheme 7):[111,112]

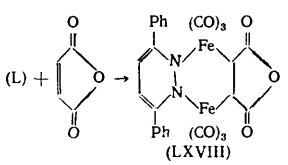
Scheme 7



It was found that complex (LXV) is readily converted into (LXVI) and the latter into (LXVII). The structures of compounds (LXVa) and (LXVIIa) (R = R′ = Ph) were confirmed by X-ray diffraction. In contrast to compounds with ligands (a) and (b), the complex obtained on the basis of benzo[*c*]cinnoline reacts with alkynes to give only a compound of type (LXV).

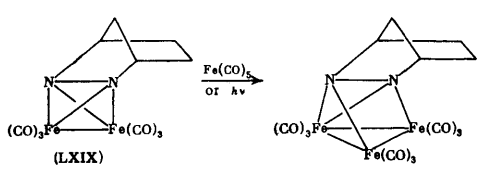
It is of interest to note that, when compounds of type (LXVII) (R = Ph) were heated *in vacuo* to 150°C, tetraphenylcyclobutadieneiron tricarbonyl was obtained. This compound can be synthesised in a single stage by heating the initial di-iron hexacarbonyl complex with a sixfold excess of diphenylacetylene (yield 70%).[111] The authors[111] noted that they were unable to obtain analogous results using aliphatic alkynes[12].

The interaction of the dinuclear complex (L) (Ar = Ph) with maleic anhydride has been assigned to reactions of the same type[113]†:



The structure of complex (LXVIII) obtained was demonstrated by X-ray diffraction[113].

Finally, a very interesting conversion into a trinuclear cluster was observed in the interaction of complex (LXIX) with $Fe(CO)_5$ or simply on its irradiation ($\lambda \geqslant 300$ nm):[51]



† Other workers[113] regard this reaction as cycloaddition.

IV. RESULTS OBTAINED BY PHYSICAL RESEARCH METHODS

The common fragment in the dinuclear complexes investigated is the group $N_2Fe_2(CO)_6$, which determines the main properties of these compounds. According to X-ray diffraction studies, the N_2Fe_2 fragment in this group has tetrahedral or a distorted tetrahedral geometry and the presence or absence of the bond between nitrogen atoms‡ in the fragment clearly divides all the complexes into two groups (see Tables 1 and 2):

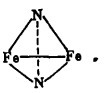
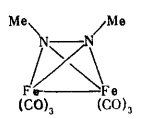
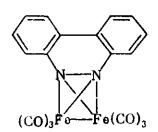
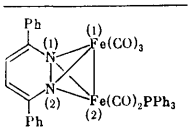
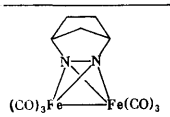


Table 1. Certain structural parameters of dinuclear complexes of type (B) (the bond lengths are quoted in angstroms and the angles in degrees).

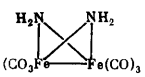
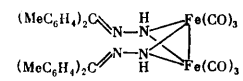
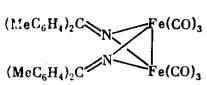
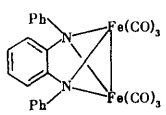
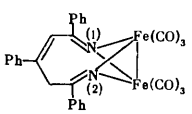
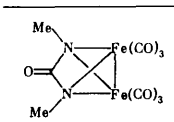
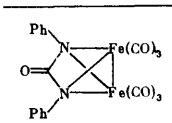
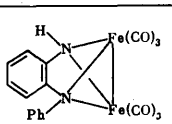
Complex	Fe—Fe	Fe—N	N—N	Fe—N—Fe	N—Fe—N	Refs.
	2.496	1.878	1.366	83.4	42.7	64
	2.508	1.914	1.399	81.9	42.90	25
	2.53	1.93($Fe_{(1)}$—$N_{(1)}$); 1.95($Fe_{(2)}$—$N_{(2)}$)	1.43	82.00	42.0	101
	2.990	1.932	1.405	81.3	43.1	121

The distance between the nitrogen atoms in dinuclear complexes with an N—N bond [(type B), Table 1] is approximately 1.40 Å, which corresponds to a single bond[44,114,115]. The distance between the nitrogen atoms in the other group of complexes [type (A), Table 2] varies in the range 2.15—2.50 Å, which undoubtedly leads to the conclusion that there is no bond between them. It has been observed that in complexes with an N—N bond the length of the Fe—Fe bond (2.50 Å) is always greater by approximately 0.1 Å than in the other group, where the Fe—Fe bond length is approximately 2.40 Å. This tendency was

‡ A dashed line NN implies that a bond between nitrogen atoms is not obligatory.

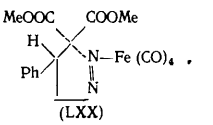
first noted by Doedens and Ibers [64] and was subsequently confirmed by Doedens [25]. The shortening of the Fe–Fe bond (to 2.40 Å) in complexes without an N–N bond is probably due to the constancy of the Fe–N bond length [116]. In the dinuclear complexes considered this bond length varies from 1.91 to 2.00 Å, but it cannot vary within limits as wide as in the case of the Fe–Fe bond [116–119]. Indeed, Table 3, taken from Vahrenkamp [116], shows that the Fe–Fe bond length can vary from 2.40 to 3.05 Å, i.e. by more than 0.6 Å. Thus, in order to keep the Fe–N bond length constant on passing from complexes of type (B) to those of type (A), the Fe–Fe bond must be somewhat shortened with a consequent obligatory decrease of the Fe–N–Fe angle (from 83° to 72°, cf. Tables 1 and 2).

Table 2. Certain structural parameters of dinuclear complexes of type (A) (the bond lengths are quoted in angstroms and the angles in degrees).

Complex	Fe–Fe	Fe–N	N–N	Fe–N–Fe	N–Fe–N	Refs.
	2.402	1.98	2.50	74.4	77.8	18
	2.40	2.00	—	—	—	44
	2.403	1.94	—	—	—	91
	2.37	2.00	—	72.50	73.00	78
	2.393	1.920 (Fe_1—N) 1.965 (F_2—N)	2.25	—	—	95
	2.39	1.975	—	75.37	65.00	19
	2.402 2.416	2.01 1.99		74 74.5	65 64.9	41 122
	2.372	2.00	2.38	72.5	72.9	79

Furthermore, the data in Table 3 show that the dependence of the Fe–Fe bond length on the Fe–heteroatom bond length is common to dinuclear iron complexes.

At the same time it is important to note that virtually identical Fe–N bond lengths have been found both in dinuclear complexes of types (A) and (B) and in iron tetracarbonyl derivatives $LFe(CO)_4$. X-Ray diffraction studies on complex (LXX) [70] showed that the Fe–N bond length in this complex is 1.979 Å and the nitrogen–nitrogen bond length is 1.242 Å, which corresponds to the N=N double bond:



(LXX)

It follows from X-ray diffraction data that the $N_2Fe_2(CO)_6$ group in the complexes considered has C_{2v} symmetry, like other structurally related bridge groups in the compounds $LFe(CO)_6$. [64]

Table 3. Certain results of the X-ray diffraction analysis of dinuclear complexes with heteroatomic bridges [116].

Complex	Bridge heteroatom	Fe–heteroatom distance, Å	Fe–Fe, Å
$[(CO)_3FeNH_2]_2$	N	1.98	2.40
$(CO)_5Fe_2Cp(PMe_2)$	P	2.19	2.63
$(CO)_8FeMnAsMe_2$	As	2.35	2.85
$[(NO)_2FeI]_2$	I	2.58	3.05

Group theoretical analysis makes it possible to predict five infrared-active vibrations for terminal carbonyl groups: $2A_1 + 2B_2 + B_1$. [120]

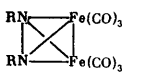
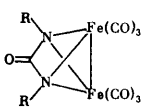
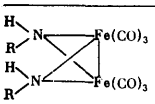
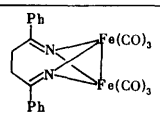
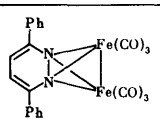
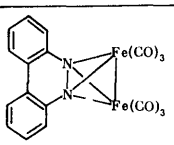
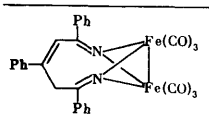
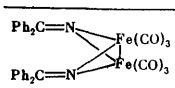
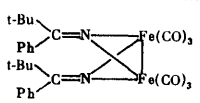
Table 4 presents the stretching vibration frequencies of the CO ligands for certain complexes containing the $N_2Fe_2(CO)_6$ group. It shows that the spectra of the majority of complexes in the region of $\nu(C{\equiv}O)$ are very similar. In a number of studies this similarity between the spectra enabled the presence of the $N_2Fe_2(CO)_6$ group in the complexes to be observed [69,92,94].

It is much more difficult to conclude whether or not the nitrogen–nitrogen bond is present on the basis of infrared spectra. In this instance the influence of the ligand as a whole is probably more important. It may consist both in the breakdown of the symmetry of the metal carbonyl fragment, which leads to an increase of the number of absorption bands [92], and in an enhancement or weakening of the electron-donating properties of the ligand, which causes a band shift [53]. Such a band shift is manifested to an even greater extent on passing to $LF_2(CO)_6$ systems with other bridge heteroatoms (S, P, As, etc.) [120].

At the same time infrared spectra of the complexes $LFe_2(CO)_7$ yield undoubtedly important information. Apart from the four stretching vibration bands of the terminal CO ligands, they include the characteristic absorption at 1820–1730 cm^{-1}, which convincingly demonstrates the presence of a carbonly bridge group [83,93]. The mass spectra of many complexes contain molecular ions

and indicate the successive elimination of all the carbonyl groups[18,53,92,108]. The fragmentation of the LFe_2^+ ions formed in this process is determined mainly by the nature of the ligand L.

Table 4. The stretching vibration frequencies of the CO ligands in certain complexes $LFe_2(CO)_6$.

Complex	ν (C=O), cm^{-1}	Refs.
 R = n-Pr R = t-Bu	2072, 2032, 1999, 1911, 1972 (sh.) 2060, 2022, 1994, 1972 (sh.)	36
 R = n-Pr R = t-Bu	2082, 2046, 2002, 1991 2082, 2045, 1998	36
 R = n-Pr R = t-Bu	2075, 2051, 2034, 1998, 1992 2066, 2047, 1033, 1992	36 36
	2070, 2030, 1995, 1975, 1960 (sh.) ($CHCl_3$)	36 36 35
	2065, 2025, 1985, 1970 (cyclohexane)	123
	2073, 2033, 1982, 1972 (CS_2)	24
	2068, 2031, 1998, 1986, 1972 (sh.), 1967 (hexane)	94
	2047, 2041, 1994, 1979 (cylcohexane)	92
	2073, 2036, 1994, 1987, 1971 (cyclohexane) сан)	92

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Lanthanide Titanates

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Compounds formed in the R_2O_3-TiO_2 binary systems, where R is a lanthanide element, are examined. Methods for the preparation of lanthanide titanates in both polycrystalline and single-crystal form are analysed. Attention is concentrated on the crystal chemistry and the physicochemical properties of lanthanide titanates with quadrivalent titanium. A number of examples of practical applications of these compounds are given.
The bibliography includes 110 references.

CONTENTS

I.	Introduction	228
II.	The synthesis of lanthanide titanates	228
III.	High-temperature interaction of titanium dioxide with lanthanide sesquioxides	230
IV.	Crystal chemistry of lanthanide titanates	232
V.	Properties of lanthanide titanates	235
VI.	Examples of practical applications	240

I. INTRODUCTION

Interest in lanthanide titanates with the pyrochlore structure arose in connection with the suggestion that they might have ferroelectric properties—by analogy with cadmium pyroniobate $Cd_2Nb_2O_7$, which has a cubic structure of the pyrochlore type and is a unique and unusual ferroelectric material at low temperatures[1,2]. This finding stimulated the study by Roth[3], who was the first to synthesise and investigate a whole series of lanthanide titanates with the pyrochlore structure. Further investigations showed that only some titanates ($La_2Ti_2O_7$ and $Nd_2Ti_2O_7$)[4,5] are effective ferroelectric substances with extremely high Curie temperatures. However, numerous studies on the synthesis and properties of these compounds raised a series of new problems. Thus an investigation of the phase transformations in the high temperature interaction of TiO_2 with lanthanide sesquioxides established the formation of lanthanide titanates with different structures from which new technological materials with a set of interesting properties can be obtained. Their high fire resistance and chemical stability permits their employment in high-temperature chemistry and nuclear power engineering.

However, the available data have not been surveyed hitherto; a monograph[6] deals with only a small range of problems. The present review gives a systematic account of data concerning the methods of synthesis, crystal chemistry, and physicochemical properties of lanthanide titanates with quadrivalent titanium; only compounds formed in the R_2O_3-TiO_2 binary systems are considered.

II. THE SYNTHESIS OF LANTHANIDE TITANATES

A series of methods for the synthesis of lanthanide titanates in the polycrystalline and single-crystal form have now been developed.

1. Solid-Phase Synthesis

The solid-phase synthesis is carried out by heating to high temperatures mechanical mixtures of TiO_2 and lanthanide sesquioxides. In most cases discs are pressed from the mechanical mixtures and are then placed on platinum supports and annealed in electric furnaces in air.

Ceramic technology requires the use of high temperatures, prolonged annealing, and in addition repeated sintering of the product in order to obtain a single-phase titanate. Nevertheless this method of synthesis is widely used[3,7-16], but only as a rule in those cases where the aim was to obtain a compound of the type $R_2Ti_2O_7$ from a mechanical mixture of the oxides having the composition $2TiO_2 + R_2O_3$. This is apparently due to the advantageous feature of the method: the fact that one obtains a product with a more precisely specified composition and also because of the fairly high rate of formation of the given compounds. For example, the compounds $La_2Ti_2O_7$, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Gd_2Ti_2O_7$, $Dy_2Ti_2O_7$, and $Y_2Ti_2O_7$ have been obtained[3] by heat treatment for 4 h at 1100°C. However, the same compounds have been synthesised at different temperatures in a number of studies. For example, $Sm_2Ti_2O_7$ has been obtained at 1200°, 1300°, and 1400°C[3,7] and $Gd_2Si_2O_7$ at 1000°, 1350° and 1400°C[3,7], the duration of sintering being determined by the temperature of the synthesis.

2. The Coprecipitation Method

Numerous investigations[7,15,17-33] in the last decade showed that it is useful to obtain polycrystalline lanthanide titanates by coprecipitation and not for mechanical mixtures of oxides. Amorphous hydroxides are as a rule coprecipitated by treating a mixture of an aqueous solution of $TiCl_4$ and a nitric acid (or hydrochloric acid) solution of R_2O_3 with aqueous ammonia. The product is filtered off, washed with water, and dried at approximately 100°C. According to X-ray and electron diffraction data, the freshly obtained precipitates are amorphous. Their characteristic feature is the presence of a considerable amount of chemically bound lanthanide hydroxide. In the general case the rate of chemical reaction between the lanthanide and titanium at the instant of precipitation depends on the nature and composition of the precipitate formed; the amount of product which has reacted may range from 15 to 45%.[31]

Crystalline titanates are formed on further heating of mixtures of the amorphous hydroxides to the crystallisation temperature. Fig. 1*c* presents a thermogram of the coprecipitated neodymium and titanium hydroxides[22]. It is seen that two peaks are characteristic of the precipitated product: an endothermic peak at 290°C corresponding to

dehydration and an exothermic peak at 810°C corresponding to the crystallisation of $Nd_2Ti_2O_7$. It has also been established [22] that the thermograms of precipitates obtained by coprecipitation differ significantly from those of the individual lanthanum and titanium hydroxides, which enabled the authors [22] to suggest that coprecipitation results in the formation of the corresponding lanthanide titanate and not simply a mechanical mixture.

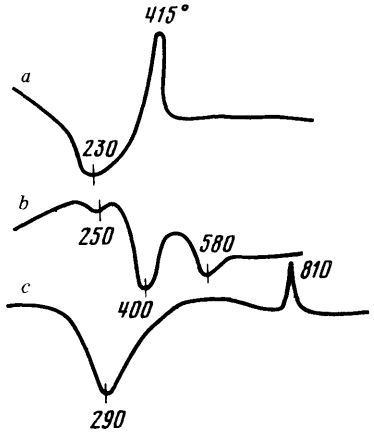


Figure 1. Thermograms: a) titanium hydroxide; b) neodymium hydroxide; c) coprecipitated neodymium and titanium hydroxides [22] (the numerals represent the temperature in °C).

A detailed study has been made [31] of the dehydration process, which showed that the products of the chemical reaction between titanium and lanthanide hydroxides are hydroxo-complexes $R_2[TiO_2(OH)_2]_3.nH_2O$. OH groups are eliminated at approximately 500°C and the residual water (1.5–2%) is lost at approximately the same temperature. The main bulk of water is eliminated at temperatures up to 150°C where the rate of dehydration is extremely high. Because of this, the authors [31] concluded that the interaction between the coprecipitated lanthanum and titanium hydroxides most probably involves the OH groups and proceeds via the hydroxo-complex stage.

The phases in the temperature range 400–800°C, i.e. from the temperature corresponding to the virtually complete removal of water up to the formation of lanthanide dititanates, have been identified [30,31]. The existence of intermediate compounds having the composition $La_{2/3}TiO_3$ having the perovskite structure and crystallising in the orthorhombic system has been established. According to the authors [31], lanthanide metatitanates are the intermediate products which are formed on heating the coprecipitated hydroxo-complexes of the lanthanide and titanium. These compounds are unstable and decompose above 800°C with formation of lanthanide dititanates. It is noteworthy that analogous defect phases having the perovskite structure have been detected earlier on interaction of La_2O_3 and TiO_2 in a reducing atmosphere [33–35]. However, the unit cell parameters of perovskite were in this case [31] somewhat smaller than in the study of Leonov et al. [35] This was explained [31] by the failure to complete the formation of the lattice in the compounds $R_{2/3}TiO_3$ obtained by the moderate heating of the coprecipitated hydroxides.

The temperature of the synthesis of lanthanide titanates is usually somewhat higher than their crystallisation temperature. Thus $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$ crystallise at 810° and 825°C, while the compounds have been synthesised by different workers in the temperature range 1000–1300°C. This is also true of the titanates of the entire lanthanide series. The degree of formation of $La_2Ti_2O_7$ has been studied [21] as a function of temperature and duration of annealing. It was established that the temperature rather than the duration of annealing has a considerable influence on the yield of $La_2Ti_2O_7$. The intensity and distinctness of the lines on the X-ray diffraction patterns increase with temperature for different durations of heat treatment in the range from 1 to 12 h, but above 1100°C they hardly change. At 900°C the complete formation of $La_2Ti_2O_7$ requires an annealing time of 6 h.

Thus the clear advantages of the coprecipitation method are a reduction of the temperature of the synthesis of the compounds and the possibility of the virtually complete binding of R_2O_3 and TiO_2, which can probably be explained by the formation of lanthanide titanates already in the coprecipitation process [22,27].

Phase transformations in the ageing of a charge comprising the coprecipitated hydroxides in air under normal conditions have also been investigated [31]. The investigation showed that the nature of the processes occurring on heating a charge of coprecipitated lanthanide and titanium hydroxides differs from that of the processes occurring during their storage, although the overall composition of the products may be the same in both cases. Thus, when the charge is heated, the chemical interaction between the components proceeds via the hydroxo-complex stage with formation of lanthanide titanates. In the second case (during the ageing of the charge) the hydroxo-complexes of the lanthanide and titanium decompose with the ultimate formation of the individual oxides R_2O_3 and TiO_2.

3. The Method Based on the Decomposition of Nitrate Salts

The technology of the synthesis of lanthanide titanates (for lanthanides ranging from La to Lu and Y) by the thermal decomposition of the nitrate salts has been described [36,37]. The starting materials were the lanthanide oxides and the salt $TiO_2(NO_3)_2.6H_2O$, which were dissolved in separate vessels in hot dilute HNO_3 solutions, which were filtered and then mixed. The resulting solutions were evaporated until the crystallisation of the salt and then heated at 500°C (5–10 h) in order to remove nitrogen. The completion of the reaction was tested by X-ray diffraction and chemical analyses.

It was established [36,37] that lanthanide titanates (2–10% yield) are formed at the instant of the decomposition of the nitrate salts. During annealing, the yield is 55–77% at 900°C and 81–90% at 1200°C. The completion of the reaction requires additional heat treatment at 1500–1600°C for 3 h; after this, the substances did not contain the free oxides. Like the coprecipitation method, the above procedure made it possible to carry out the initial stage of the synthesis at lower temperatures, but in addition it eliminates the operation of filtration and washing of the precipitates.

4. Synthesis of Lanthanide Single Crystals

In the synthesis of lanthanide single crystals the main problem is the attainment of the melting point (approximately 2000°C), which requires a complex apparatus; the problems of the selection of crucibles and the atmosphere for the synthesis are no less important.

According to the literature[38-51], lanthanide titanate single crystals are synthesised by a wide variety of methods, both high-temperature (the Verneuil method, zone fusion, etc.) and low-temperature (hydrothermal, in solution, and in the melt) methods.

(a) High-temperature methods. The Verneuil method, which consists in passing a fine powder of the initial substance through the flame of an oxygen–hydrogen burner, can apparently be regarded as the main high-temperature method for the growing of lanthanide titanate single crystals. After fusion in the flame, droplets of the substance fall on to the upper part of the growing crystal. Crystallisation can begin either on portions of the prefused and crystallised substance or (preferably) on a seed crystal introduced beforehand[52]. La_2TiO_5 [38] and $Nd_2Ti_2O_7$ [46] have been obtained in this way.

In the course of its application to the synthesis of single crystals from refractory oxides the Verneuil method has undergone a series of changes. The improvements involve mainly the heating apparatus. A plasma or electric arc furnace has replaced the oxygen burner. Nd_2TiO_5 [39] and $La_2Ti_2O_7$ [44] single crystals have been grown by the Verneuil method in combination with a plasma furnace.

A vertical version of the zone fusion method (or the floating zone method), which eliminates the possibility of the contamination of the product by the substance of the boat, has been used[4,53] to grow $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals. Heating was achieved with the aid of a reflection furnace. The crystal is grown by moving the fused zone down a rod of the initial substance clamped at both ends. The quality of the crystal is determined mainly by the rate of migration of the zone. $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals were grown at zone velocities of 10 and 5 mm h^{-1} respectively.

Among the high-temperature methods for the growing of lanthanide titanate single crystals, the method of direct high-frequency fusion in a cold container, developed at the Lebedev Physical Institute of the USSR Academy of Sciences[54], merits attention. The technological process includes three stages: (1) the preparation of the "seed" melt, which can be achieved by means of an additional source of heat; (2) gradual fusion under the influence of a high-frequency field of the entire charge with the exception of a thin layer directly adjoining the water-cooled walls of the container; (3) slow directional crystallisation of the melt by a gradual decrease of the power of the high-frequency generator or by lowering the container relative to the inductor[54]. The fundamental advantage of the new technology is the absence of contact between the melt and chemically different materials, which ensures a high chemical purity of the product.

Single crystals of almost all the lanthanide titanates, having the general formula $R_2Ti_2O_7$ (except for R = Ce or Pm), have been synthesised in this way[55]. The size of the crystals was 2–12 mm, which enabled the authors to investigate a whole series of their physicochemical properties.

(b) Low-temperature methods. Preference has been given recently to low-temperature methods in which crystals are grown during deposition from solution. Depending on the nature of the solvent, different versions of the method are possible. In a non-aqueous solvent crystals are grown from solution in the melt; if the solvent is water, then the hydrothermal method, based on a high-pressure technique, is suitable for refractory oxides insoluble in water at atmospheric pressure[52]. The following titanates have been obtained by growing from solution in the melt; $R_2Ti_2O_7$ (R = Sm, Eu, Gd, Tb, Ho, Er, or Y)[40,47,48,49]; R_2TiO_5 (R = Dy or Gd);[40] $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$.[50]

Titanates of the type $R_2Ti_2O_7$ have been synthesised[40] in platinum crucibles with closely fitting lids at a constant temperature of 1235°C in the course of 1 week (in order to concentrate the solution by evaporating the solvent); lead oxide PbO was used as a flux. The isotropic crystals obtained had a well-defined octahedral shape (with a diameter of 3 mm). Another variety of the method was used in the same study[40] to synthesise single crystals of the type R_2TiO_5: an increase of the concentration of the solution was achieved by its slow cooling from 1280° to 940°C at a rate of 3 K h^{-1}. Analysis showed that the crystals obtained (lamellar or rod like, up to 3 mm in length) contained 4% of PbO as an impurity. The same variety of the method—slow cooling until the formation of a saturated solution—was used in other studies[47,49,50]. However, careful study of the crystals obtained by Weissenberg's method[50] revealed the occurrence of twinning in the crystals, which significantly hindered their further structural investigation.

The hydrothermal method for the growing of lanthanide titanate crystals has been used in only two studies[32,42] for the synthesis of single crystals of the type R_2TiO_5 (R = Nd, Sm, Dy, or Yb). Mechanical mixtures with the ratio $TiO_2:R_2O_3 = 1:1$, placed in silver tubes, were put in exoclaves of the type designed by Sternberg. The synthesis was carried out over a period of 50–100 h at 700°C and 1000–2000 atm. The solvent was an aqueous 8% NH_4F solution. The crystals obtained were prismatic and their size ranged from 0.1 to 0.5 mm. Shcherbakova et al.[42] also quote the calculated lattice parameters of Nd_2TiO_5, which agree well with other published values for this compound[39]. The small size of the crystals of other titanates R_2TiO_5 precluded structural investigation.

In conclusion one should note yet another method, used[41] to prepare Y_2TiO_5 single crystals. The method is based on the solid-phase reaction between Y_2O_3, TiO_2, and sodium oxalate, which occurs at 1300°C in a sealed tube; the $NaYTiO_4$ formed, having a structure of the K_2NiF_4 type, decomposes on further heating in air at 1500°C and is a heterogeneous product containing a certain number of very small transparent acicular Y_2TiO_5 crystals.

III. HIGH-TEMPERATURE INTERACTION OF TITANIUM DIOXIDE WITH LANTHANIDE SESQUIOXIDES

The interaction of TiO_2 with lanthanide sesquioxides in systems where R = La, Gd, Dy, Er, Yb, or Y has now been investigated in greatest detail; phase diagrams have been constructed for these systems[11,14,15,19,57-59]. The interaction of TiO_2 with other lanthanide oxides has been scarcely investigated; data are available only concerning the isolation in a pure state of certain individual phases.

It is noteworthy that the phase diagrams of the TiO_2–R_2O_3 systems are fairly complex and, despite common features, differ significantly for different lanthanides. As an illustration, one may consider the phase diagrams of the TiO_2–Gd_2O_3, TiO_2–Y_2O_3, TiO_2–Er_2O_3, and TiO_2–Yb_2O_3 systems (Figs. 2–5). Evidently the compounds $R_2Ti_2O_7$, typical for all the remaining lanthanides, exist in the range of compositions close to 33 mole % R_2O_3. However, their crystal structures are not the same; in the range from samarium to lutetium and yttrium the $R_2Ti_2O_7$ structure is cubic and of the pyrochlore type (space group $Fd\,3m$); $La_2Ti_2O_7$, $Nd_2Ti_2O_7$, and $Pr_2Ti_2O_7$ crystallise in the monoclinic system (space group $P2_1$). According to a number of data[57,58,60,61], $Gd_2Ti_2O_7$, $Y_2Ti_2O_7$, $Er_2Ti_2O_7$, and $Tb_2Ti_2O_7$ melt congruently, at 1820° C, > 1900°, 1980°, and 1860° C respectively.

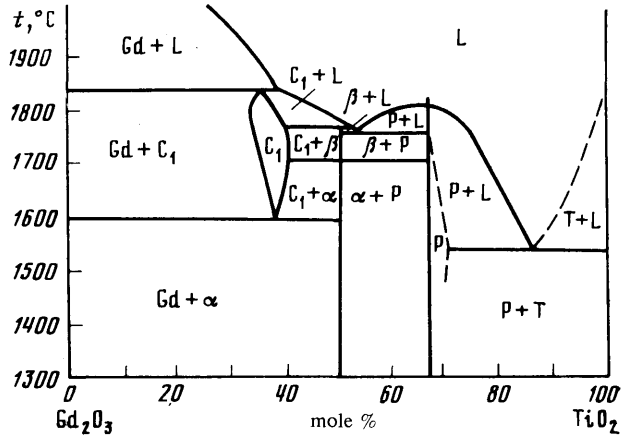


Figure 2. Phase diagram for the Gd_2O_3–TiO_2 system[14]; notation: Gd = Gd_2O_3 (solid solution); T = TiO_2 (solid solution); P = $Gd_2Ti_2O_7$ (pyrochlore); α and β = low- and high-temperature forms of Gd_2TiO_5; C_1 = face-centred cubic solid solution; L = liquid.

The differences between the ionic radii of the elements in the lanthanide series do not apparently influence the region of homogeneity for different $R_2Ti_2O_7$. The smaller scope for the substitution by titanium of "large" lanthanide ions in the range from lanthanum to gadolinium, associated with this fact, leads either to the formation of narrower regions of homogeneity (for example, approximately 3–5 mole % for $Gd_2Ti_2O_7$) or to their complete absence ($La_2Ti_2O_7$). With decrease of ionic radius, the width of the regions of homogeneity of the compounds $R_2Ti_2O_7$ grows, reaching 12 mole % for $Yb_2Tb_2O_7$. The considerable expansion of the region of homogeneity of the phases with the pyrochlore structure in the Dy_2O_3–TiO_2 and Y_2O_3–TiO_2 systems[19,57] at temperatures $\gtrsim$ 1700° C apparently indicates the influence in this case of factors other than the size factor. Figs. 2 and 3 show that the composition with 50 mole % R_2O_3 in the given systems corresponds to the compounds Gd_2TiO_5 and Y_2TiO_5. Compounds of a similar type (R_2TiO_5) are also characteristic of the entire series of lanthanides and as a rule exist in two polymorphic forms: the low-temperature orthorhombic α-form and the high-temperature hexagonal β-form. Only the high-temperature modification of Er_2TiO_5 has a cubic structure of the fluorite type[58]. However, according to the data of Leban et al.,[56] the compound Er_2TiO_5 was not detected in the study of the phase transformation in the Er_2O_3–TiO_2 system in the temperature range 1500–1600° C. Instead two cubic solid solutions of the pyrochlore and fluorite type, undergoing an interconversion at 50 mole % Er_2O_3, were found. The similarity of the structural types of the cubic phases formed at high temperatures in this system was apparently reflected in the interpretation of the data[56,58] and requires further elucidation and investigation of the system.

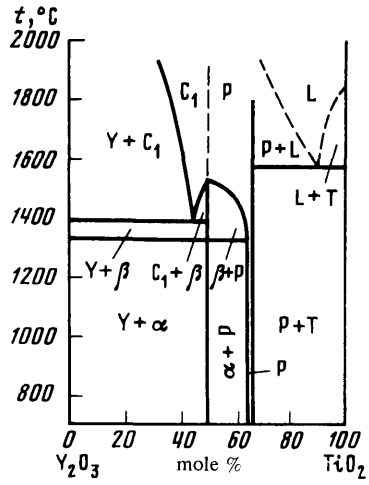


Figure 3. Phase diagram for the Y_2O_3–TiO_2 system[57]; notation: Y = Y_2O_3 (solid solution); T = TiO_2 (solid solution); P = $Y_2Ti_2O_7$ (pyrochlore); α and β = low- and high-temperature forms of Y_2TiO_5; C_1 = cubic solid solution with the fluorite structure; L = liquid.

It is of interest to note a difference in the behaviour of R_2TiO_5 at high temperatures as a function of the nature of the lanthanide[11,14,19,57,58,59]. Thus La_2TiO_5 is a stoichiometric compound, which melts congruently; Gd_2TiO_5 melts incongruently; Dy_2TiO_5 and Y_2TiO_5 are converted at high temperatures into a solid solution of the pyrochlore or fluorite type respectively and the phase diagram of the Yb_2O_3–TiO_2 system altogether fails to reveal the existence of the compound Yb_2TiO_5, as can be seen from Fig. 5. The compounds $2La_2O_3.9TiO_2$ and Yb_6TiO_{11}, which do not arise in other systems, also exist in the La_2O_3–TiO_2 and Yb_2O_3–TiO_2 systems (with the maximum and minimum ionic radii of the lanthanide).

All the diagrams presented in the regions of compositions where the R_2O_3 content reaches up to 33 mole % correspond to simple eutectic systems (the eutectic temperatures and compositions are listed in Table 1). When the R_2O_3 content exceeds 50 mole %, there is a broad region of a cubic solid solution of the fluorite type (C_1), the lattice parameters of these solutions being a function of composition. The existence of a narrow single-phase

region (~ 1 mole %) of a cubic solid solution having a structure of the type $Tl_2O_3(C_2)$ has been noted only for R = Dy, Er, or Yb.

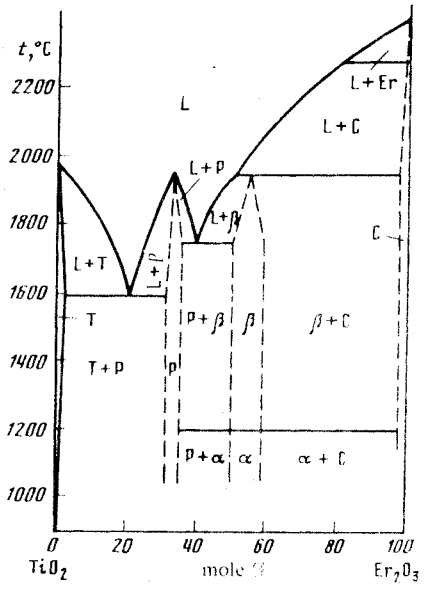


Figure 4. Phase diagram for the Er_2O_3–TiO_2 system[58]; notation: Er = Er_2O_3 (solid solution); T = TiO_2 (solid solution); P = $Er_2Ti_2O_7$ (pyrochlore); α and β = low- and high-temperature forms of Er_2TiO_5; C = solid solution of Mn_2O_3 type; L = liquid.

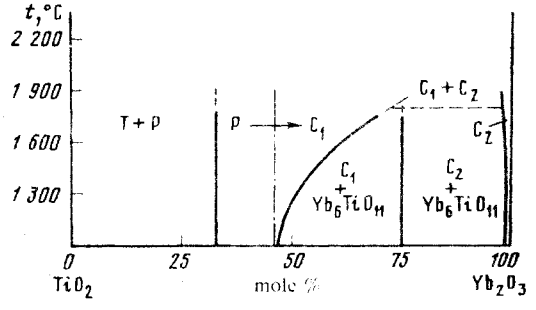


Figure 5. Phase diagram for the Yb_2O_3–TiO_2 system[59]; notation: P = $Yb_2Ti_2O_7$ (pyrochlore); T = TiO_2 (solid solution); C_1 = cubic solid solution with the fluorite structure; C_2 = cubic solid solution of the Tl_2O_3 type.

The presence of such narrow regions of solid solutions was established in the Er_2O_3–TiO_2 system[58] only in connection with the study of a diffusion-dependent interaction involving single-crystal specimens. The diffusion research technique, first used for the TiO_2–Er_2O_3 and TiO_2–Y_2O_3 systems[58,62], undoubtedly made it possible to obtain more complete information about the characteristics of the high-temperature interaction in oxide systems.

IV. CRYSTAL CHEMISTRY OF LANTHANIDE TITANATES

In the first studies[3,13] which initiated the systematic investigation of systems based on TiO_2 and R_2O_3 it was already established that many mixtures of these oxides, taken in proportions of 2 : 1, give rise to the compounds $R_2Ti_2O_7$ with a pyrochlore type structure after appropriate heat treatment. It was found in later investigations[3,19,33,63] that such compounds do indeed exist for lanthanides whose ionic radius satisfies the condition $1.22 < (r_{R^{3+}}/r_{Ti^{4+}}) < 1.5$.

Table 1. The eutectic temperatures and compositions in the R_2O_3–TiO_2 systems.

Composition	Eutectic compn. mole % R_2O_3	Eutectic temp., °C	Refs.
Gd_2O_3–TiO_2	13	1540	51
Tb_2O_3–TiO_2	14	1640	51
Er_2O_3–TiO_2	22	1550	58
Yb_2O_3–TiO_2	10	1580	59

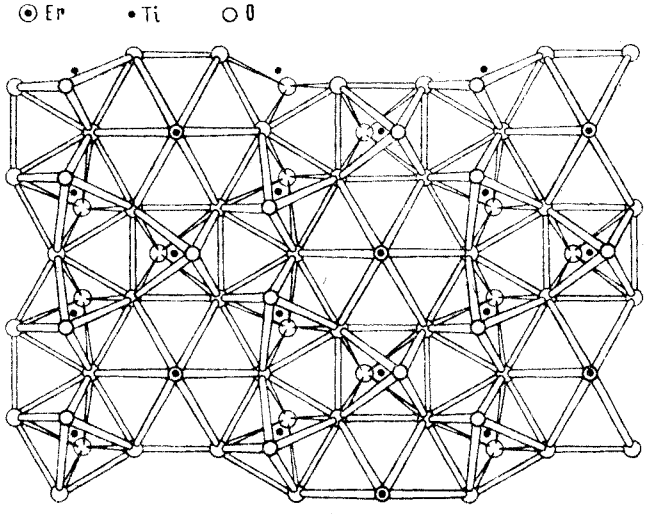


Figure 6. Projection of the pyrochlore structure ($Er_2Ti_2O_7$)[66] along a threefold symmetry axis.

This geometrical criterion, based on analysis of the ionic radius ratios from the standpoint of the theory of close packing, is defective according to some workers[64], because the interatomic interaction in pyrochlores is not purely ionic. However, for lanthanide titanates this criterion gives rise to no doubts. Thus in the $Nd_2O_3 + 2TiO_2$ composition, for which $r_{R^{3+}}/r_{Ti^{4+}} = 1.52$, there is no pyrochlore phase and the compound $Nd_2Ti_2O_7$ crystallises in the monoclinic system. This is also true of $La_2Ti_2O_7$. The remaining lanthanides (from samarium to lutetium) give rise to cubic $R_2Ti_2O_7$ structures of the pyrochlore

type[7-10,16,18,19,36,47,65-68]. There is also a linear correlation between the unit cell parameter a and the ionic radius $r_{R^{3+}}$.

The compounds $R_2Ti_2O_7$ (R represents elements from samarium to lutetium and yttrium) have the same structures as the mineral pyrochlore $NaCaNbTaO_6F$ with the structural formula $A_2B_2O_7$, where A represents sodium and calcium ions and B represents niobium and tantalum ions. Pyrochlore has a face-centred cubic lattice (space group $Fd3m$). The pyrochlore structure is derived[69] from the fluorite structure. When the fluorite structure is converted into the pyrochlore structure, one of each eight oxygen ions is removed from the anionic lattice sites, while the remaining ions are somewhat displaced from their ideal positions. The large A ions are coordinated to eight oxygen ions, which surround them, being located at the vertices of a distorted cube. The pyrochlore structure consists of a three-dimensional skeleton of distorted BO_6 octahedra joined together by their vertices. Series of mutually parallel chains joined by their vertices alternate with series of mutually parallel chains perpendicular to the chains of the first series. The octahedra of neighbouring chains are also joined together via their vertices (Fig. 6). The A ions and one seventh of the oxygen ions, which have not been displaced to the skeleton from the octahedra, are accommodated in the gaps between the octahedra.

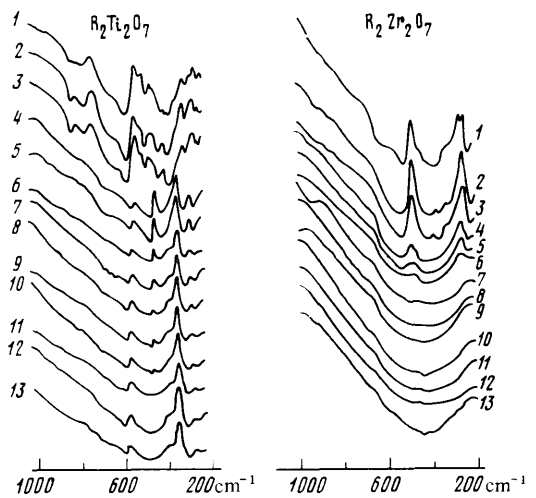


Figure 7. Infrared spectra of lanthanide titanates ($R_2Ti_2O_7$) and zirconates ($R_2Zr_2O_7$)[63]; R: 1) La; 2) Pr; 3) Nd; 4) Sm; 5) Eu; 6) Gd; 7) Tb; 8) Dy; 9) Ho; 10) Er; 11) Tm; 12) Yb; 13) Lu.

The transition from the fluorite structure to the pyrochlore structure is accompanied by the appearance on the X-ray diffraction patterns of superstructure lines corresponding to the establishment of order in the arrangement of the cations and the distortion of the oxygen polyhedra[65,67,69]. The ordering of pyrochlore phases is also indicated by the absorption maxima in the infrared spectra. Fig. 7 presents for comparison the infrared spectra of $R_2Ti_2O_7$ and $R_2Zr_2O_7$. In ZrO_2–R_2O_3 systems only certain compounds have the pyrochlore structure (R = Gd, Eu, Sm, Nd, Pr, or La). For lanthanide ions whose radii are smaller than the ionic radius of gadolinium, an ordered phase is not formed and Fig. 7 shows that in this case the infrared spectra are of a completely different type[63].

A characteristic feature of the phases of the pyrochlore type is their non-stoichiometry, which arises, on the one hand, when some of the Ti^{4+} ions are substituted by R^{3+} ions (this entails the formation of additional vacancies in the anionic sublattice), and, on the other, when some of the R^{3+} ions are replaced by Ti^{4+} ions. The general formula of the pyrochlore phases can be written as follows: $R_{2\pm x}Ti_{2\mp x}O_{7\mp x/2}\square_{1\pm x/2}$.[19]

In the series of lanthanide titanates, the $Er_2Ti_2O_7$ and $Y_2Ti_2O_7$ structures have been investigated most thoroughly[49,66] by X-ray and neutron diffraction methods (Fig. 6). The $Er_2Ti_2O_7$ unit cell contains 16 erbium ions at sites of trigonal symmetry. Each erbium ion is surrounded by 8 oxygen atoms, two of which lie diametrically opposite and are at a distance of 2.185 Å from the erbium ion, while the other six are arranged in the vicinity of the equatorial plane at a distance of 2.471 Å. The erbium ion in localised at the [common?] vertex of two diametrically opposite tetrahedra comprising erbium ions and in this respect the ions are equivalent, i.e. each erbium ion has six nearest neighbours at a distance of 3.562 Å. The Er–O–Er angle is 109°.

As mentioned above, compounds of the type $R_2Ti_2O_7$ are known also for the first members of the lanthanide series from lanthanum to neodymium (for which $r_{R^{3+}}/r_{Ti^{4+}} < 1.2$). However, in contrast to the compounds described above, which have a cubic structure of the pyrochlore type, they have a lower symmetry. This was indicated in an early study[3], where the X-ray diffraction patterns for these compounds were obtained for the first time. The infrared spectra of the compounds $La_2Ti_2O_7$, $PrTi_2O_7$, and $Nd_2Ti_2O_7$ also illustrate the difference between their crystal structure and that of pyrochlore. However, the structures of these compounds were elucidated significantly later[50] when $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals were obtained. It was found that the crystals have a monoclinic structure with the space group $P2_1/m$; the lattice parameters are listed in Table 2.

Table 2. The unit cell parameters of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$.[50]

Compound	a, Å	b, Å	c, Å	β	V, Å³
$La_2Ti_2O_7$	7.80±0.01	5.54±0.01	13.01±0.02	98°37′±10′	556
$Nd_2Ti_2O_7$	7.68±0.01	5.46±0.01	12.99±0.02	98°30′±10′	559

It has also been shown[50] that the above compounds are isomorphous with $Ca_2Nb_2O_7$ and that their lattice consists of slightly distorted perovskite blocks. However, these results required further confirmation, since the Weisenberg diagrams revealed twinning of the single crystals investigated. Subsequent studies[43,44] led to two different

interpretations. Thus the $La_2Ti_2O_7$ structure was interpreted[44] on the basis of orthorhombic symmetry; according to Gasperin's data[43], $La_2Ti_2O_7$ has a monoclinic structure close to the orthorhombic structure (and for this reason called by the authors pseudo-orthorhombic) with the space group $P2_1/m$ or $P2_1$. The latter structure can be regarded as consisting of TiO_6 octahedra joined together via their vertices. The presence of planes parallel to the (010) plane and dividing the structure into layers comprising four octahedra between which La atoms are accommodated is also typical.

Also of interest is a study[70] where it was noted that, since the crystal lattice parameters of pyrochlore vary linearly with the ionic radius, extrapolation can yield the parameters a_1 and a_2 which the compounds $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ would have had if their structure had been of the pyrochlore type. The results ($a_1 = 10.418$ Å, $V_1 = 565.4$ Å^3, and $a_2 = 10.286$ Å, $V_2 = 544$ Å^3) showed that under these conditions the volumes V_1 and V_2 are greater than for monoclinic symmetry. Hence the authors[70] concluded that heat treatment under pressure may promote the appearance of the monoclinic form of the compounds $R_2Ti_2O_7$, which are cubic under the usual conditions. The first experiments on $Sm_2Ti_2O_7$, carried out by the quenching method under pressure ($p = 54$ kbar, $t = 1390°$C), showed that the X-ray diffraction pattern obtained is no longer characteristic of pyrochlores, and may be interpreted on the basis of monoclinic or orthorhombic symmetry.

Table 3. The unit cell parameters of compounds of the type R_2TiO_5.

Compound	Structure	a, Å	b, Å	c, Å	β	Refs.
La_2TiO_5	orthorhombic	10.97	11.37	3.937	—	51
Nd_2TiO_5	orthorhombic	10.720	11.361	3.840	—	39
Sm_2TiO_5*	orthorhombic	10.59	3.792	11.351	—	9
Eu_2TiO_5*	monoclinic	15.82	5.34	15.76	92°29′	60
Gd_2TiO_5	monoclinic	15.75	5.32	15.73	87°34′	24, 60
Gd_2TiO_5	monoclinic	15.49	5.25	15.28	87°39′	19
Gd_2TiO_5	hexagonal	3.683	—	11.995	—	14
Gd_2TiO_5	orthorhombic	10.61	11.27	3.73	—	40
Dy_2TiO_5	monoclinic	15.56	5.26	15.35	87°38′	19, 24
Dy_2TiO_5	orthorhombic	10.49	11.26	3.70	—	40
Y_2TiO_5	monoclinic	15.75	5.32	15.73	87°34′	19
Y_2TiO_5	orthorhombic	10.35	3.70	11.25	—	41

*Sm_2TiO_5 and Eu_2TiO_5 were obtained in the study of the phase diagrams of R–O–Ti ternary systems.

Such studies appear promising for the synthesis of compounds of low symmetry with new properties (for example, ferroelectric properties), which the given compounds did not possess in the cubic phase. However, preliminary experiments for the heat treatment of $Dy_2Ti_2O_7$ and $Tb_2Ti_2O_7$ under pressure showed that the pyrochlore structures are fairly stable and for this reason the transition to the monoclinic form of compounds with lanthanide ionic radii smaller than $r_{Sm^{3+}}$ requires fairly high pressures and temperatures (in excess of 2000 °C and 70 kbar).

Studies in recent years[14–16,19–24,38–42,57,58] showed the presence in the R_2O_3–TiO_2 systems also of phases other than those described, namely compounds of the type R_2TiO_5 for the oxide ratio $TiO_2 : R_2O_3 = 1 : 1$. The first of these was obtained[11,24,29] for R = La, Gd, or Dy. Nowadays compounds of this type are known for R = La, Nd, Sm, Eu, Gd, Dy, Er, or Y.

The existence of two R_2TiO_5 modifications—the low-temperature orthorhombic modification (α) and the high-temperature hexagonal modification (β)—apparently created certain difficulties for the determination of the structure and because of this there was no unanimous view on this problem. The X-ray diffraction patterns of the compounds R_2TiO_5 were interpreted[24,60] on the basis of a monoclinic lattice, which was regarded as derived from the fluorite lattice. The unit cell parameters of compounds of the type R_2TiO_5 obtained hitherto are listed in Table 3.

The most detailed structural studies on compounds having the general formula R_2TiO_5 have been made in Refs. 38, 39, 41, and 51. Müller-Buschbaum and Scheunemann[39] examined the structure on the basis of an Nd_2TiO_5 single crystal. The unit cell contains four Nd_2TiO_5 formula units. Structures of this type have characteristic coordination numbers and coordination polyhedra made up of lanthanide and titanium atoms. The lanthanide atoms are surrounded by seven oxygen atoms ($n = 7$), six of which make up a distorted octahedron. A skeleton of octahedra joined together via their faces and nodes is formed, each two octahedra, located along the [001] face with $z = 1/4$ and $z = 3/4$, being joined via the seventh, common oxygen ion. This characteristic seventh ion constitutes simultaneously a vertex and is part of the base of a trigonal pyramid made up of oxygen ions around the Ti^{4+} ion. The same polyhedra as in the hexagonal form A of the pure sesquioxide Nd_2O_3 are distributed in the three-dimensional structure around the neodymium atom.

A coordination number of five, which is characteristic of Ti^{4+}, is observed only in the above compounds and in K_2TiO_5. The crystal structure of Nd_2TiO_5 is analogous to that adopted[41] for Y_2TiO_5. All other lanthanide titanates having the general formula R_2TiO_5 are also isomorphous with Y_2TiO_5 [41,71] and their structures constitute a fairly rare example of the coexistence of 7- and 5-coordination of ions. The unusual 5-coordination for the titanium ion is also noted in a study[71], where the compounds R_2TiO_5 (R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, or Y) were investigated by infrared and Raman spectroscopy. Two experimental features characteristic of these compounds were noted in particular[71]:

1. In the region of low frequencies (< 350 cm^{-1}) those corresponding to the absorption bands in the infrared spectrum and to the peaks in the Raman spectrum are correlated with the ionic radius of the lanthanide, i.e. as a rule are sensitive to the mass of the tervalent cations R^{3+}.

2. Sharp infrared absorption bands and the most intense peaks in the Raman spectrum are observed in the frequency range 775–875 cm^{-1}. These are unusually high frequencies; thus in compounds of the type β-Ba_2TiO_4 with 4-coordinate titanium the frequencies assigned to the vibrations of the TiO_4 polyhedra are in the range 690–750 cm^{-1}; in compounds with 6-coordination (Sr_2TiO_4) the frequencies are in the range 550–625 cm^{-1}. In order to account for the presence of peaks at such high frequencies in the R_2TiO_5 spectra, a comparison was made[71] with the infrared spectra of the compounds $KTiOPO_4$ and $RbTiOPO_4$ in which titanium atoms are surrounded by six oxygen atoms but one of the Ti–O bonds is shorter than the others. In these compounds the same infrared frequencies (775–850 cm^{-1}), associated with the Ti–O vibrations are observed. On the basis of this analogy, the author concluded that the vibrational frequencies in the R_2TiO_5 spectra, located

above 350 cm^{-1}, refer to the internal vibrations of the TiO_5 groups and that the highest-frequency peaks are due to the fact that one oxygen atom in the TiO_5 polyhedron differs structurally from the other four oxygen atoms. Because of this, one of the Ti–O distances is shorter than the others, which alters the vibration frequency associated with the TiO_5 group.

V. PROPERTIES OF LANTHANIDE TITANATES

The physicochemical properties of lanthanide titanates of type $R_2Ti_2O_7$ have been investigated in a number of studies. Table 5 presents the melting points, densities, thermal expansion coefficients α, refractive indices n, and the microhardness values H_μ of the compounds $R_2Ti_2O_7$, measured for both polycrystalline[36] and single-crystal[55] specimens. It shows that all the above characteristics as a rule increase with increasing atomic number of the elements. It has been stated[55] that the experimental densities of compounds of the pyrochlore type agree satisfactorily with the values estimated from the lattice parameter. We may note that, whereas the difference between the densities of single-crystal and polycrystalline materials is small, the microhardness of the single crystals obtained by Ershova et al.[55] is significantly higher than for polycrystalline compounds. The crystals also have a higher refractive index.

Table 4. Certain properties of compounds of the type $R_2Ti_2O_7$.

Compound	Colour	Density, g cm^{-3}		M.p., °C (Ref.36)	$10^6\alpha$, K^{-1} (Ref.36)*	n (Ref.55)	H_μ, kgf mm^{-2}	
		Ref.36	Ref.55				Ref.36	Ref.55
$La_2Ti_2O_7$	white	5.71	—	1650	9.46	—	400	—
$Pr_2Ti_2O_7$	green	—	5.73	1560	—	—	—	648
$Nd_2Ti_2O_7$	lilac	5.77	6.10	1650	9.80	—	—	712
$Sm_2Ti_2O_7$	white	6.06	6.20	1630	10.16	2.21	850	1103
$Eu_2Ti_2O_7$	white	—	6.29	1650	10.70	2.27	720	1104
$Gd_2Ti_2O_7$	white	6.41	6.50	1740	10.29	2.36	720	1114
$Tb_2Ti_2O_7$	cream	6.54	6.59	—	10.35	2.38	780	1122
$Dy_2Ti_2O_7$	white	6.52	6.76	1730	10.31	2.39	720	1152
$Ho_2Ti_2O_7$	cream	6.75	6.81	1820	10.25	2.41	660	1198
$Er_2Ti_2O_7$	pink	6.81	6.91	1780	10.66	2.47	850	1202
$Tm_2Ti_2O_7$	white	6.95	7.07	1820	10.41	2.48	1030	1232
$Yb_2Ti_2O_7$	white	7.12	7.21	1890	10.9	2.51	1140	1264
$Lu_2Ti_2O_7$	white	—	7.27	—	9.87	2.57	—	1293
$Y_2Ti_2O_7$	white	4.66	4.83	2000	10.46	2.34	—	1099

*In the temperature range 20–800°C.

There have been fairly numerous studies on the EPR spectra of lanthanide titanates with the pyrochlore structure[72,73], the luminescence and transmission spectra[74,75], the Mössbauer effect, and the Gol'danskii–Karyagin effect[76] in the Mössbauer spectra of compounds of the type $R_2Ti_2O_7$.[77–82] Thus the wavelength range in which the $Er_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Gd_2Ti_2O_7$, and $La_2Ti_2O_7$ crystals are virtually transparent (0.3–15 μm) has been determined[75]. The characteristics of the quadrupole interaction and the spin–lattice relaxation in $Dy_2Ti_2O_7$ at temperatures $\leq 750°C$ have been published[77]. The isomer shift and the effective field at the Gd^{3+} nucleus in $Gd_2Ti_2O_7$ have been determined[78]. The study of $Gd_2Ti_2O_7$ and $Er_2Ti_2O_7$ [80–82] revealed a significant contribution of the Gol'danskii–Karyagin effect due to the asymmetry of the quadrupole doublets in the Mössbauer spectrum. These results indicate a considerable anisotropy of the vibrations of the lanthanide atoms in the titanate lattices. Thus the application of Mössbauer spectroscopy in the study of lanthanide titanates established their dynamic structures (i.e. the characteristics of various atomic motions in the molecules and crystals of substances in this class) and hence made it possible to supplement significantly the results of X-ray diffraction studies, which reveal the "static" structure of crystals[83].

Studies devoted to the magnetic and electrical properties of lanthanide titanates merit much attention.

1. Magnetic Properties

The study of the magnetic properties of the pyrochlore-type compounds $R_2Ti_2O_7$ (R = Gd, Tb, Dy, Ho, Er, Yb, or Nd) with a cubic structure showed that antiferromagnetic ordering takes place in many of them only at very low temperatures[84–89] ($T_N \simeq 1.5$ K).

It is clear from the standpoint of the crystal structure that the magnetic behaviour of the lanthanide ion in titanates with the pyrochlore structure must be similar to that observed in oxides[90] and lanthanide gallate garnets[91], where the closest distances between lanthanide ions are respectively 2.66 and 3.8 Å and the magnetic interaction is relatively weak (the Er–Er distance in $Er_2Ti_2O_7$ is approximately 3.562 Å).

The first measurements of the magnetic susceptibility as well as experiments on the adiabatic demagnetisation of certain compounds $R_2Ti_2O_7$ (R = Gd, Dy, Ho, or Er) with the pyrochlore structure were carried out by van Geuns[84]. In the experimental temperature range (2–80 K) all the compounds proved to be paramagnetic; above 8 K the magnetic susceptibility obeys satisfactorily the Curie–Weiss law with a Curie constant which agrees to within 10% with the theoretical value for the free ion. However, deviations from the Curie–Weiss law are observed for $Dy_2Ti_2O_7$ and $Gd_2Ti_2O_7$ below 8 K. Measurements on the magnetically diluted compound $Dy_{0.2}Y_{1.8}Ti_2O_7$ showed that in this case the deviations of the $\chi^{-1}(T)$ relation from linearity decrease and the Curie–Weiss law holds down to 2 K. This justifies the conclusion that the observed deviations arise mainly as a result of exchange interaction between lanthanide ions. It was shown[84] that the small Curie–Weiss constant and the relatively high ionic density make the compounds suitable for the attainment of low temperatures by the method of adiabatic demagnetisation. This stimulated a number of more detailed studies[88,92,93] on magnetisation and magnetic entropy as a function of temperature and external field.

Apart from the applied aspect described above, the interest in lanthanide titanates is due to the fact that, by virtue of their simple cubic structure they are convenient physical objects for testing various models of the theory of the magnetism of lanthanide compounds. In this connection mention should be made of a study[85] where the magnetic susceptibilities of $Dy_{0.2}Y_{1.8}Ti_2O_7$ and $Yb_2Ti_2O_7$ were examined theoretically. Measurements of the heat capacities of the double oxides $R_2Ti_2O_7$ (R = Dy, Er, or Yb) at ultralow temperatures are of special interest[86].

The principal data on the magnetic properties of the compounds $R_2Ti_2O_7$ (R = Gd, Tb, Dy, Ho, Er, Yb, or Nd), obtained in the above investigations and by Cashion et al.[87] and Mamsurova et al.,[89] are given below.

(a) $Dy_2Ti_2O_7$. According to Flood[88], $Dy_2Ti_2O_7$ passes to the antiferromagnetic state at $T_N = 1.4$ K, which agrees with $T_N = 1.35$ K found for single crystals[87]. The effective magnetic moment $\mu_{eff} = 9.6\ \mu_B$ obtained[88] is close to

$\mu_{eff} = g\sqrt{J(J+1)} = 10.63\ \mu_B$ for the free ion. However, it follows from the measurements of susceptibility at ultra-low temperatures[86] that χ decreases almost to zero when $T \to 0$. This indicates the anisotropy of the properties of $Dy_2Ti_2O_7$. Furthermore, the observed changes in entropy at low temperatures ($\Delta S_{magn} \simeq R \ln 2$) are inconsistent with the higher degeneracy (more than by a factor of 2) of the ground state[86].

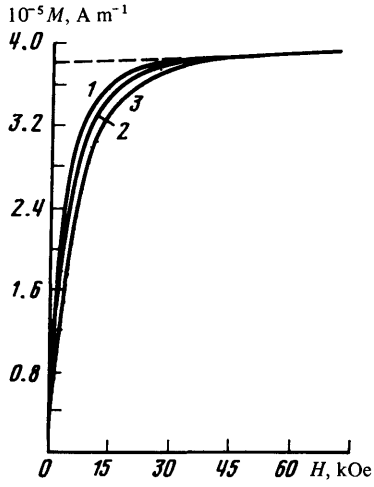


Figure 8. Dependence of the magnetisation of $Dy_2Ti_2O_7$ on the external field[88]; temperature (K): 1) 2.18; 2) 2.95; 3) 4.2.

The crystal field generated at the lattice sites occupied by lanthanide ions due to the 8 nearest oxygen ions is known[49,66] to have a predominantly axial symmetry. The deviation of the positions of the lanthanide ions from cubic symmetry is also greater than that in garnets[66], where the g-factor has been shown[91] to be significantly anisotropic, particularly for Dy and Er. Townsend and Crossley[85] calculated the corresponding parameters of the crystal field and obtained in this way the theoretical susceptibility curve for the magnetically dilute compound $Dy_{0.2}Y_{1.8}Ti_2O_7$ and compared it with experiment. This enabled them to conclude that the ground state of Dy^{3+} consists of a pure Kramers doublet with a projection of the overall moment $J_z = \pm 15/2$. For the pure state with $J_z = \pm 15/2$, there exists only one direction corresponding to easy magnetisation in the single-crystal material, which implies that $g_\perp = 0$ and $g_\parallel = 20$. It is then found that, for high values of J, the susceptibility of the powder is always close to the values for the free ion, since $J^2 \simeq J(J+1)$. However, the saturation magnetisation of the powder should be smaller than for the free ions. This was demonstrated by measuring the magnetisation in strong fields[88]. Fig. 8 illustrates the dependence of the magnetisation on the field strength for several temperatures[88]. The saturation magnetisation obtained is smaller by a factor of 2 than was expected for the isotropic case and agrees well with the fact that the ground state of the Dy^{3+} ion is represented by an orbital doublet: the experimental data presented in Fig. 8 yield $n_B = 9.4$ (where n_B is the number of Bohr magnetons per ion); on the other hand, if the ground state is represented by a pure doublet, then the theoretical values $n_B = g_\parallel J' = 10$. The small difference between these values arises apparently because the wave function for the ground state contains terms due to an admixture of excited levels (Van Vleck paramagnetism).

The absolute magnetic entropy was obtained in the same study[88] as a function of temperature and the external magnetic field. The results show that the compound $Dy_2Ti_2O_7$ can be used as the working substance in the magnetic cooling cycle in the temperature range between the boiling points of liquid hydrogen and liquid helium.

(b) $Yb_2Ti_2O_7$. Fig. 9 presents the temperature dependence of the reciprocal of the susceptibility for $Yb_2Ti_2O_7$ according to the results of Townsend and Crossley[85]. The curve exhibits a significant deviation from linearity, which the authors attribute to the influence of the crystal field. The ground state $^2F_{7/2}$ of the free Yb^{3+} ion is split by the cubic field into three levels Γ_7, Γ_8, and Γ_6. As a result of trigonal distortion, Γ_8 is split further into two Kramers doublets Γ_6 and Γ_7. The authors[85] showed that Γ_7 is the ground state. They calculated the crystal field parameters and the energy gaps $\Gamma_6 - \Gamma_7 = 1040$ cm^{-1} and $\Gamma_8 - \Gamma_7 = 530$ cm^{-1}. The theoretical magnetic susceptibility curves agree well with experiment (Fig. 9).

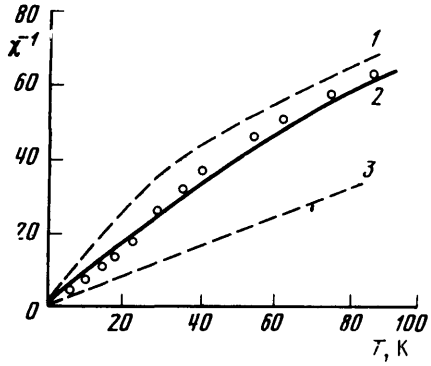


Figure 9. Temperature dependence of the reciprocal of the magnetic susceptibility of $Yb_2Ti_2O_7$;[85] the circles represent experimental points: 1) and 2) theoretical curves with different crystal field parameters; 3) free ion.

Certain parameters of the crystal field obtained[94] from the analysis of the Mössbauer spectra for ^{170}Yb in $Yb_2Ti_2O_7$ made it possible to explain the weak quadrupole interaction in this compound.

The heat capacity curve, illustrated in Fig. 10,[86] exhibits a singularity at 0.214 K, which apparently corresponds to the transition to the antiferromagnetic state. The observed entropy change $\Delta S/R = 0.693 = \ln 2$ corresponds to a Kramers doublet as the lowest state.

The exchange integrals $|J/k| = 1.2$–1.4 K (k is the Boltzmann constant), the nuclear contribution to the heat capacity, $C_{hfs}T^2/R = 0.00011K^2$, and the g-factors ($g = 2.1$–2.4) have been estimated[86].

(c) $Er_2Ti_2O_7$. According to Blote et al.,[86] the heat capacity of $Er_2Ti_2O_7$ exhibits a distinct λ-anomaly at T_N = 1.25 K. The entropy change determined from the heat capacity curves $\Delta S = 0.675R \simeq 0.97 \ln 2$. Consequently the singularity in the heat capacity is presumably due to long-range magnetic ordering (with a Kramers doublet as the ground state). The slope of the $\chi^{-1}(T)$ curve, measured by van Geuns[84] for powdered specimens, corresponds to the slope of the analogous curve for the free ion, while according to Blote et al.[86] the slope is smaller by a factor of approximately 3.5 over the limited temperature range 1.4–4 K. The latter may correspond to $g = 5.5$ if only the Kramers doublet is populated. van Geuns obtained a high Curie–Weiss constant $\theta = 22$ K, the high value of which cannot be due to magnetic interaction. Blote et al.[86] claim that this can be explained by assuming that the Er^{3+} ion has a doublet 10 cm^{-1} above the ground state; the combined effect of the two doublets then makes the susceptibility of the powdered specimen approximately the same as that of the free ions. Estimation of the exchange interaction integrals[86] yields $|J/k| = 0.56–0.63$ K.

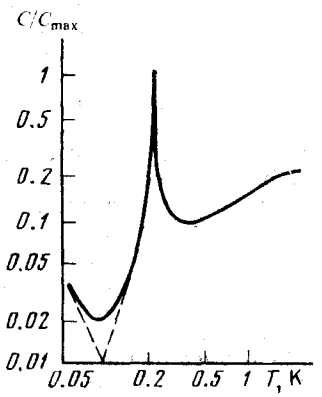


Figure 10. Temperature dependence of the heat capacity of $Yb_2Ti_2O_7$ [86] (left-hand dashed line—nuclear contribution to the heat capacity).

(d) $Gd_2Ti_2O_7$. The splittings of the energy levels in the crystal field for the Gd^{3+} ion with the ground state $^8S_{7/2}$ ($L = 0$) are very small and the magnetic properties of the ion are presumably the same as those of the 8-fold degenerate ground state. Fig. 11 (curve *4*) shows that the susceptibility of $Gd_2Ti_2O_7$ is independent of temperature below 4 K.[87]

(e) $Ho_2Ti_2O_7$ and $Tb_2Ti_2O_7$. The Ho^{3+} and Tb^{3+} ions have an even number of 4*f* electrons. Because of this, their ground state is not a Kramers doublet but two singlets separated by a small gap. The magnitude of the gap enters directly into the expression for the magnetic susceptibility, determines T_N, etc. However, there are no detailed literature data for $Ho_2Ti_2O_7$ and $Tb_2Ti_2O_7$. Fig. 11 (curves *1* and *3*)[87] illustrates the $\chi(T)$ relations for these compounds. The susceptibility of $Ho_2Ti_2O_7$ follows a simple Curie law with $\chi = C/T$ and exhibits an antiferromagnetic transition at $T_N = 1.3$ K. The Curie constant C corresponds to the value for the free ion but can be accounted for (as for $Dy_2Ti_2O_7$) also by the non-Kramers pair discussed above, when $g_\parallel = 20$ and $g_\perp = 0$ (or $\langle J_Z \rangle = \pm 8$).

(f) $Nd_2Ti_2O_7$. Neodymium dititanate belongs to the class of compounds for the magnetic properties of which there are still no literature data. As already mentioned, in contrast to the majority of compounds of the type $R_2Ti_2O_7$, $Nd_2Ti_2O_7$ has a monoclinic structure[50] (space group $P2_1/m$; $z = 4$).

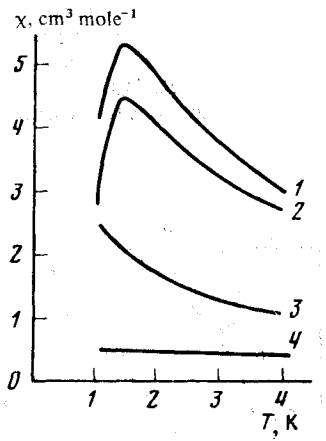


Figure 11. Temperature dependence of the magnetic susceptibilities of different lanthanide titanates: 1) $Ho_2Ti_2O_7$; 2) $Dy_2Ti_2O_7$; 3) $Tb_2Ti_2O_7$; 4) $Gd_2Ti_2O_7$.[87]

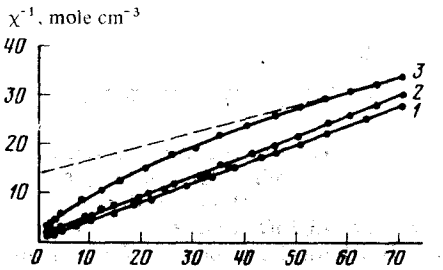


Figure 12. Temperature dependence of χ^{-1} of the compounds $Nd_2Ti_2O_7$ [1) for specimen cut out along the direction of easy magnetisation; 2) for powdered specimen] and Nd_2TiO_5 (curve *3*).

We measured the low-temperature susceptibility of $Nd_2Ti_2O_7$ (in the temperature range 1.6–70 K) and the magnetisation in the field of a superconducting solenoid (up to 55 kOe)[89]. Fig. 12 (curves *1* and *2*) shows that the compound remains paramagnetic up to 1.6 K. The Curie–Weiss law holds over the entire experimental temperature range with the parameters $C = 2.44$ $cm^3 K$ $mole^{-1}$ and $\theta = -3$ K. The value of C obtained yields $\mu_{eff} = 3.12$ μ_B for the effective magnetic moment of Nd^{3+}, which is close to the value for the free ion.

It is noteworthy that the observed values of θ apparently reflect the influence of the crystal field on the orbital moment of $4f$ electrons rather than of the exchange interaction between Nd^{3+} ions. The tenfold degenerate level of the free Nd^{3+} ion is known to be split into five doublets in crystal fields whose symmetry is lower than cubic. Since the Curie–Weiss law holds for $Nd_2Ti_2O_7$ over the entire experimental temperature range, presumably the ground state of the Nd^{3+} ion in this compound (the Kramers doublet) is fairly remote from the nearest excited levels, which are not populated even at 70 K. In this case an effective moment $J' = 1/2$ and $g = \mu_{eff}/\sqrt{J(J+1)} = 3.6$ can be attributed to the Nd^{3+} ion in $Nd_2Ti_2O_7$.[89]

It is noteworthy that all the studies mentioned above were carried out using powdered specimens, which significantly restricts the scope of the magnetic measurements. An exception is the study of Cashion et al.,[87] who used for the investigation very small $R_2Ti_2O_7$ and R_2TiO_5 crystals, but, as already stated, they contained impurities.

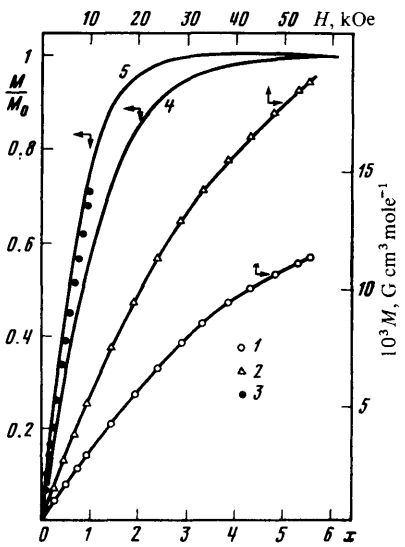


Figure 13. Dependence of the magnetisation on the external field for the compounds $Nd_2Ti_2O_7$ [1) powdered specimen; 2) specimen cut out along the direction of easy magnetisation] and Nd_2TiO_5 (curve *3*). Curves *4* and *5* represent the Brillouin functions for $J = 1/2$ and $J = 1$.

We attempted[89] to investigate a cylindrical $Nd_2Ti_2O_7$ specimen, consisting of small coalesced acicular single crystals, in which the crystallographic directions of all the crystals coincided. The susceptibility and the magnetisation of the specimens along this direction proved to be greater than for the powdered specimen. Although in the maximum field of 55 kOe the magnetisation does not reach saturation (Fig. 13), the nature of the $M(H)$ relations suggests that the saturation magnetisations for the two different $Nd_2Ti_2O_7$ specimens are different. Evidently, the anisotropy in $Nd_2Ti_2O_7$ is of a single-ion type and is manifested in the given case in terms of the anisotropy of the g-factor.

In the same study[89] measurements were made on a polycrystalline Nd_2TiO_5 specimen. Fig. 12 (curve *3*) shows that the Curie–Weiss law does not hold in this case, in contrast to $Nd_2Ti_2O_7$. The slope of the $\chi^{-1}(T)$ curve in the region of 60 K and above corresponds to $\mu_{eff} = 3.54\ \mu_B$, i.e. approaches the value for the free ion. Under these conditions, θ becomes greater than the usual value ($\theta = -45$ K). Since the substance remains paramagnetic down to 1.6 K, θ is evidently determined by the influence of the crystal field.

With decrease of temperature, the slope of the curve changes and $\mu_{eff} = 2.03\ \mu_B$ in the range 1.6–4.2 K. It is natural to suppose that at such low temperatures only the lowest Kramers doublet is populated; the effective value is then $J' = 1/2$ and $g = \mu_{eff}/\sqrt{J(J+1)} = 2.3$. This is confirmed by measurements of the magnetisation of Nd_2TiO_5 in fields up to 55 kOe. Fig. 13 presents the results of measurements as a plot of the relative magnetisation M/M_0 against $x = g\mu_B JH/kT$, where $T = 4.2$ K, $g = 2.3$, $J = 1/2$, and $M_0 = 2\,Ng\mu_B J = 12.84$ CGSM units $mole^{-1}$ (N is the Avogadro number). Evidently the points obtained lie closer to the theoretical Brillouin function of x for $J = 1/2$ and for $J = 1$.

Consequently in the compound Nd_2TiO_5, which has orthorhombic symmetry, the internal crystal field splits the tenfold degenerate ground state of the free Nd^{3+} ion in such a way that the distance between the levels is not as large as in $Nd_2Ti_2O_7$ and, when the temperature is raised from 1.6 to 60 K, all the sublevels of the ground multiplet are populated.

The magnetic properties of other lanthanide titanates of the type R_2TiO_5 can be regarded as virtually uninvestigated. Only one report[87], where the measurements of the magnetic susceptibilities of Gd_2TiO_5 and Dy_2TiO_5 are presented for the temperature range 1–4 K, mentions that the specimens apparently undergo a transition to an antiferromagnetic phase at 1.25 and 1.55 K respectively.

Isomorphous substitution of one set of magnetic atoms by another, which is allowed by the structure of the compounds R_2TiO_5, can significantly increase the phase transition temperature and can also alter other magnetic characteristics of the substance[95]. A study of the magnetic susceptibility of single-crystal $NdFeTiO_5$ in which some of the Nd^{3+} ions have been replaced by Fe^{3+} ions revealed the occurrence of antiferromagnetic ordering at $T_N = 18.5 \pm 0.5$ K. T_N is determined in this case by the cooperative ordering of the spin system of the Fe^{3+} ions. The Nd^{3+} ions remain paramagnetic below T_N, but their magnetic moments are polarised owing to interaction with the Fe^{3+} spin. The principal characteristics of the temperature dependence of the magnetic susceptibility can be explained on the hypothesis that there is interaction between the ordered spins of the Fe^{3+} ions and the electrons populating the lowest Kramers doublet in the Nd^{3+} ions[95].

2. Electrical Properties

The resistivities of all the lanthanide titanates, including scandium and yttrium titanates, were measured for the first time at room temperature and those of certain titanates ($La_2Ti_2O_7$, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Er_2Ti_2O_7$) at a higher temperature (up to 1000°C) by Brixner[8] in 1964. The resistivity at room temperature was approximately $10^{12}\ \Omega$cm [the lower resistivity ($\sim 10^{10}\ \Omega$cm) obtained for three compounds, with cerium, praseodymium, and terbium, was explained by the author as due to the loss of oxygen by the specimens during heat treatment in an

inert atmosphere]. The order of magnitude of the resistivity apparently shows that ionic conduction, due to the diffusion of ions, predominates, which is characteristic of a defect pyrochlore structure[69]. On raising the temperature to 1000°C, the resistivity falls exponentially to 10^2 Ω cm (Fig. 14). Thus the compounds investigated are *p*-type semiconductors, which means that at high temperatures the electronic mechanism of conduction becomes dominant.

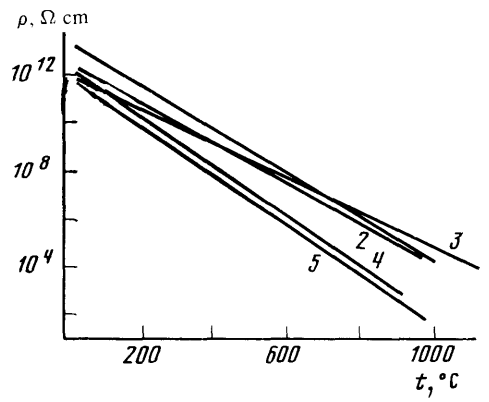


Figure 14. Temperature dependence of the electrical conductivities of lanthanide titanates: 1) $La_2Ti_2O_7$; 2) $Nd_2Ti_2O_7$; 3) $Ho_2Ti_2O_7$; 4) $Sm_2Ti_2O_7$; 5) $Er_2Ti_2O_7$.[8]

The temperature dependence of the dielectric constants of all the titanates has been measured[8]. The author notes the extremely high values of the constants ($\epsilon \simeq 30$–40) at room temperature. The measurement of the temperature dependence of ϵ was undertaken in the hope of observing ferroelectric properties in the compounds investigated. However, the measurements showed that the dielectric constant hardly changes with temperature below room temperature and increases somewhat when the temperature is raised further. The author[8] correctly attributes this increase of ϵ to the exponential decrease of the resistivity of the specimen and not to its ferroelectric behaviour.

The search for ferroelectric materials among complex oxides with a pyrochlore structure has been prosecuted for many years, apparently in connection with the discovery in 1952 of a low-temperature ferroelectric modification of the compound $Cd_2Nb_2O_7$,[1] which has the pyrochlore structure at room temperature. It was found that the properties of this compound differ from those of all other ferroelectrics and are so unusual that they attracted attention to the entire class of compounds of the pyrochlore type[2-4]. It might have been expected that other ferroelectrics with similar structure would have interesting properties. The existence in the pyrochlore-type structure of octahedra distributed in a specified manner and joined together via their vertices (this arrangement is most favourable for the manifestation of ferroelectric properties[2]) makes it very similar to a perovskite type structure, many representatives of which are typical ferroelectrics. After considering chains of oxygen tetrahedra in a pyrochlore type structure, Megaw[96] concluded that cadmium pyroniobate might also have ferroelectric properties.

Nevertheless $Cd_2Nb_2O_7$ is so far the only ferroelectric with the pyrochlore structure which has been investigated in detail, although broad maxima on the curves relating ϵ and tan δ to temperature have been observed for a number of pyrochlore compounds. According to the authors, they are associated with ferroelectric and antiferroelectric transitions[97,98]. Attempts to detect ferroelectricity in a series of lanthanide titanates with the pyrochlore structure were again undertaken in 1969.[7] However, measurements of the dielectric constants of $Sm_2Ti_2O_7$ and $Er_2Ti_2O_7$ in the range from room temperature to the helium temperature also failed to detect ferroelectric transitions.

The existence in the $R_2Ti_2O_7$ series of compounds with a symmetry lower than cubic (R = La, Nd, or Pr) stimulated further investigation of their dielectric properties[4,53]. Monoclinic crystals are known to belong to the class of polar crystals. Very careful studies enabled Nanamatsu et al.[5] to announce that lanthanum titanate ($La_2Ti_2O_7$) is a new ferroelectric with an extremely high Curie temperature, one of the highest among all known ferroelectrics. Similar properties were also discovered in an $Nd_2Ti_2O_7$ single crystal[4].

A hysteresis loop has been observed[4] in the curve relating the electric [dielectric?] shift to the field strength at room temperature in a strong electric field of approximately 300 kV cm^{-1}. The spontaneous polarisation and the coercive field were obtained from these measurements. Ferroelectric domains have been observed in $Nd_2Ti_2O_7$ single crystals when the latter were etched in boiling aqueous nitric acid. The crystals thus grown proved to consist of a single domain; pyroelectricity was clearly revealed along the *b* axis at room temperature and its polarity could be altered by applying to the specimen an electric field of 370 kV cm^{-1}.

Table 5. Ferroelectric, electro-optical, and piezoelectric properties of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$ single crystals.

Parameter	$La_2Ti_2O_7$ (Ref.5)	$Nd_2Ti_2O_7$ (Ref.4)
Size of single crystal	d = 5 mm, l = 50 mm	d = 5 mm, l = 30 mm
Melting point, °C	1790	1800
Crystal lattice	monoclinic	monoclinic
Space group	C_2^2—$P2_1$	C_2^2—$P2_1$
Density, g cm^{-3}	5.79	6.08
Curie temperature, °C	1500	>1500
Spontaneous polarisation, μC cm^{-2}	5	9
Coercive field, kV cm^{-1}	45	200
Dielectric constants (at a frequency of 1 kHz)		
ϵ_{11}	52	31
ϵ_{22}	62	43
ϵ_{33}	42	47
Quality coefficient $1/\epsilon V_\pi^2$, V^{-2}	$27 \cdot 10^{-7}$	$24 \cdot 10^{-9}$
Electromechanical coupling factor k_{22}	0.29	0.15
Piezoelectric constants d_{22}	$16 \cdot 10^{-12}$	$6.5 \cdot 10^{-12}$
Elasticity constant s_{22}	$5.5 \cdot 10^{-12}$	$4.8 \cdot 10^{-12}$

Measurement of the temperature dependence of the dielectric constant of $Nd_2Ti_2O_7$ revealed no anomalies in the range from room temperature to 1500°C. The authors[4] therefore suggested that the Curie point of this specimen lies above 1500°C.

The data obtained by Nanamatsu and coworkers[4,5] are presented in Table 5. The investigations led to the conclusion that both compounds ($La_2Ti_2O_7$ and $Nd_2Ti_2O_7$) are

ferroelectrics with high coercive fields at room temperature and high Curie points; the observed excellent electro-optical and piezoelectric properties of these compounds may be useful for their practical applications.

Similar studies have not so far been made on compounds of the type R_2TiO_5, although they should apparently exhibit dielectric properties of the same type. This was pointed out by the authors of an early investigation [11], who believed that the similarity of the dielectric properties of the compounds $La_2O_3.TiO_2$ and $La_2O_3.2TiO_2$ follows from plots of the temperature variation of tan δ and (Fig. 15).

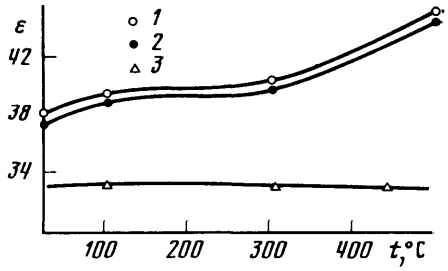


Figure 15. Temperature dependence of the dielectric constants ε (at a frequency of 1 MHz) of three binary compounds [11]: 1) $La_2O_3.TiO_2$; 2) $La_2O_3.2TiO_2$; 3) $2La_2O_3.9TiO_2$.

VI. EXAMPLES OF PRACTICAL APPLICATIONS

The possibility of using lanthanide titanates as dielectrics has been discussed in the literature for a long time. As early as 1946, mixtures of lanthanide oxides, including lanthanum and titanium oxides, were patented [99] as suitable for use in condensers as a dielectric layer with a weak temperature dependence of the dielectric constant.

The development of radioengineering industry and the requirement for new materials with optimal parameters stimulated a number of recent studies [100-106], designed to discover ceramic dielectric compositions suitable for various condensers. The dielectric properties of $La_2Ti_2O_7$ proved to be extremely useful for such purposes. Thus a new dielectric ceramic having the composition $(La_2Ti_2O_7)_{1-\alpha}(Sr_2Nb_2O_7)\alpha$, where $0 < \alpha \leq 0.85$, has been reported [100,101] as suitable for condensers with temperature compensation. This ceramic has a high value of ε, low dielectric losses, and a weak temperature dependence of the dielectric constant. It has been mentioned in almost all the investigations that the addition of different amounts of $La_2Ti_2O_7$, up to 1.2 mole %, to ceramic materials of different composition significantly decreases the temperature dependence of the dielectric constant and improves the properties of the materials.

The ceramic containing 35–50 mole % $PbTiO_3$, 25–35 mole % $SrTiO_3$, 4.5–15 mole % $CaTiO_3$, 3–20 mole % Bi_2O_3, 0.5–20 mole % TiO_2, and 4–12 mole % $La_2Ti_2O_7$ is a material which can be used successfully in a high-voltage condenser [103]. Its dielectric constant is unusually high ($\epsilon = 1850$) and the breakdown potential is 14 kV mm^{-1}.

It has been shown [107,108] that $La_2Ti_2O_7$ can also be used in condensers for the preparation of transistors on thin films of complex structure. A special method for the manufacture of such films has been developed [108].

Yet another aspect of the applications of lanthanide titanates is associated with $Eu_2Ti_2O_7$. Europium is an element suitable for the control of excess reactivity in nuclear reactors because it has a high thermal neutron absorption cross-section and resistance to damage by radiation [109]. The oxide Eu_2O_3 can be used for the same purpose. However, tests for resistance to corrosion carried out in water at 250°C and a pressure of 45.5 atm [110] showed that the best results are obtained when europium and titanium are combined ($Fu_2Ti_2O_7$). The chemical stability of this material, its properties, and behaviour under intense incident radiation have been discussed [109].

The development of laser technology has been accompanied by continuously growing requirements for laser crystals. A high thermal stability and chemical purity, optical transparency, and mechanical strength are qualities characteristic of lanthanide titanates which may prove useful in laser research. Analysis of the transmission spectra quoted [75] for $Er_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Gd_2Ti_2O_7$, and $La_2Ti_2O_7$ demonstrated the suitability of these materials as matrices for various lanthanide additives in the preparation of crystals for infrared lasers.

As already mentioned above, the compounds under consideration can be used successfully as the working substances in the attainment of low temperatures by adiabatic demagnetisation.

Presumably further studies on lanthanide titanates (especially R_2TiO_5) may significantly supplement our knowledge of their physicochemical properties and hence extend significantly the limits of their practical applications.

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Non-stoichiometry of the Alkaline Earth Metal Oxides

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Experimental data on the departure from stoichiometry in the alkaline earth metal oxides (MO) have been summarised and analysed. The $p-T-x$ diagram of BaO, and the equilibrium diagrams of the intrinsic atom defects in BaO and SrO, have been constructed. The relationship between the properties of the surface of MO crystals and their ability to emit electrons has been examined. The bibliography contains 94 references.

CONTENTS

I.	Introduction	243
II.	Experimental data on the departure from stoichiometry in alkaline earth metal oxides	243
III.	Some thermodynamic properties of MO crystals	248
IV.	Nature of the intrinsic atom defects in MO	254
V.	Properties of the surface and nature of the emitting power of MO crystals	257

I. INTRODUCTION

The alkaline earth metal oxides (MO) are widely used as electron-emitting coatings on thermionic-cathodes, and have been the objects of a large number of physico-chemical studies. The properties of the alkaline earth metal oxides, such as the ability to emit electrons, electrical conductivity, photo-conductivity, luminescence, etc., are extremely sensitive to change in the composition of the MO, that is to departures from stoichiometry. Thus studies of the dependence of the composition of non-stoichiometric MO crystals on the thermodynamic parameters of the state of the "crystal–vapour" system carried out in the past ten years in the Soviet Union and in other countries are of considerable theoretical and practical importance.

The present review summarises available experimental data on the direct determination of the departure from stoichiometry, and compares and analyses the data in order to build up from the isolated fragments, as far as possible, a more complete picture of the state of MO crystals in equilibrium with their vapour. The summary and analysis of the experimental data are also important in relation to the general questions of the chemistry of non-stoichiometric crystals and the problems of investigating the nature of the strong emitting power of MO crystals.

II. EXPERIMENTAL DATA ON THE DEPARTURE FROM STOICHIOMETRY IN ALKALINE EARTH METAL OXIDES

Thermodynamic analysis of the phenomena arising in the distribution of the components of a crystal between the vapour and solid phases shows that a certain quantity of M and O must be present in MO crystals and on their surface in a state different from the usual state of M and O forming the crystal of the compound and occupying regular sites of the crystal lattice. This difference is revealed, in particular, in the difference in the chemical properties of these states of the metal and oxygen in their reactions with water, acids, etc. These components of the MO will subsequently be described as excess if the concentration of one of them is greater than that of the other or quasi-excess if they are equal, irrespective of the location of these components in the crystal. The differences in the chemical and physicochemical properties of the excess components have made it possible to develop methods for their direct quantitative determination[1-8].

1. Excess Metal in MO. Influence of the Surface of the Crystals on the Concentration of Excess Metal in a Non-stoichiometric Specimen

The study of the phenomena leading to the production of an excess of metal in MO began with attempts to determine the factors responsible for the high emitting power of oxide cathodes. A large number of studies in the Soviet Union[1,9-14] and other countries[15-20] showed that the high electron emission of oxide cathodes is in fact due to the production of excess M in the bulk and on the surface of the oxide crystals. The technical difficulties associated with studies of real cathodes, however, made it impossible to obtain reliable quantitative data on the dependence of the equilibrium concentration of the excess metal in MO on the conditions of synthesis of the material, in particular the vapour pressure and temperature. These data were obtained in the study of the physico-chemical properties of the pure oxides away from the cathodes.

The solubility of Ba in the bulk of BaO crystals was first measured in 1937 by Schriel[2], and later by Kane[3] and Libowitz[4], who by chemical analysis measured the excess Ba in BaO crystals grown from a solution of BaO in liquid Ba. According to Schriel, the solubility of Ba in BaO at 1150° is 0.5–1.2 at.%. Libowitz[4] believes that this value is slightly too high, because of experimental errors in the determination of Ba. Kane[3] and Libowitz[4] found that at 890–910° the solubility is 0.07–0.12 at.%.

Studies of importance for understanding the formation of non-stoichiometric MO crystals were carried out using single crystals grown from the vapour phase[3-6,21,22]. In particular, it was shown[5,21,22] that the excess Ba in BaO creates two types of impurity centre, corresponding to two peaks in the absorption spectra, at 2.0 eV (blue crystals) and at 1.2 eV (red crystals). Red BaO crystals were obtained by heating colourless BaO crystals in liquid Ba, and blue crystals by heating in Ba vapour. Timmer[6] found that the concentration of colour centres with an absorption maximum at 2.0 eV, calculated using Smakula's

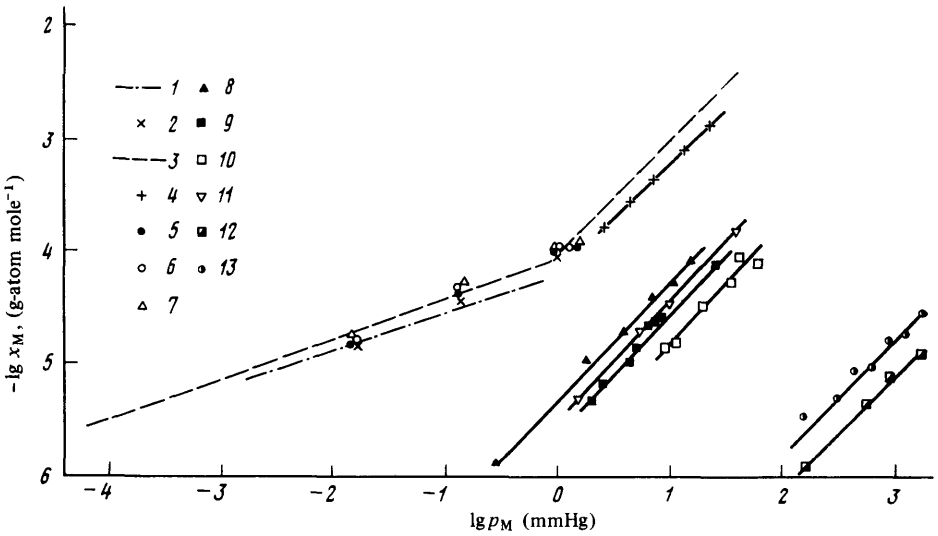


Figure 1. Solubility of excess metal in MO. Solubility isotherms for Ba in BaO at 1150° (*1*—from Ref. 6, *2*—from Ref. 29), at 1200° (*3*—from Ref. 39, *4*—from Ref. 40), at 1250° (*5*—from Ref. 29), at 1350° (*6*—from Ref. 29), and at 1450° (*7*—from Ref. 29). Solubility isotherms for Sr in SrO [28] (*8*— at 1143°, *9*—at 1238°, *10*—at 1320°). Solubility isotherm for Ca in CaO [29] (*11*) at 1700°). Solubility isotherms for Mg in MgO [29] (*12*—at 1612°, *13*—at 1813°).

equation[23], is proportional to the vapour pressure of Ba to the power 1/3. Chemical analysis of the excess Ba in blue BaO crystals[5] showed that its concentration is approximately equal to the concentration of colour centres. Thus Timmer's results were taken to indicate that the solubility of excess Ba in BaO depends on the Ba vapour pressure. The solubility isotherm obtained by Timmer at 1150°, corrected using new data on the vapour pressure of Ba, [24,25] is given in Fig. 1.

Hensley and coworkers[8,26-29] used the same experimental techniques as Timmer to study the non-stoichiometry of MO. The absorption spectra of additively coloured crystals of MgO, CaO, SrO, and BaO showed two impurity absorption bands analogous to those observed by Sproull and coworkers[5]. For the more intense of the two bands, the concentrations of the colour centres were calculated using the equations of Dexter[30] and Smakula[23]. For MgO, [26] CaO, [27] and SrO [28] these were the bands at longer wavelengths, corresponding to photon energies 5.0, 3.1, and 2.5 eV respectively, and for BaO it was the band at shorter wavelength (2.0 eV). The results of the calculations are given in Fig. 1. According to these data, the concentration of colour centres is proportional to p_M to the first power for MgO, CaO, and SrO, and for BaO the exponent lies between 1/2 and 1/3. BaO, [29] SrO, [28] and MgO [26] were studied at several temperatures, to obtain the temperature dependence of the concentration of colour centres. For BaO and MgO, the concentration of colour centres increased slightly with temperature in the range studied, 1150–1450°, and for SrO it decreased.

In the study of the formation of non-stoichiometric crystals, it must be borne in mind that the thermodynamic properties of the crystals are different in the bulk and on the surface of the crystals, that is at the "solid–gas" interface. As a result, the concentration of excess component is different on the surface and in the bulk of the crystals. For single crystals, or large crystals in general, the contribution of the excess component localised on the surface to the total departure from stoichiometry will be negligible. It will be expected to increase, considerably, however, on going to specimens having highly developed surfaces, that is powders. In 1962, the present author[10,31,32] in fact found that in powdered specimens synthesised by heating to equilibrium at 1150° in oxygen at a pressure of 10^{-8} mmHg, not less than 90% of the total excess Ba produced in the crystals was localised on the surface of the crystallites, the average size of which was several microns. The preferential localisation of Ba on the surface of powdered BaO was also established in later work[33]. Approximately the same picture was observed on zinc oxide[34,35].

This phenomenon was studied in detail for BaO and SrO, [36,37] using powdered oxide specimens prepared by the same methods[10,31,32], having a specific surface of 0.6 m^2 g^{-1}. The excess metal was determined by the gas-volumetric method first proposed by Berdennikova[1]. The substance was dissolved in water, and the quantity of hydrogen liberated in the reaction of the excess metal with water was determined. The improved method of measurement gave the analysis a sensitivity of 2×10^{-8} g-atom Ba per mole of BaO. The BaO and SrO specimens were heated for prolonged periods at 1000–1150° and $p_{O_2} = 3\times10^{-8}$–1×10^{-5} mmHg until equilibrium was established. Analysis showed that the product contained excess metal. The isothermal dependence of the concentration of excess metal on p_M (p_M was calculated from the given oxygen pressure and the known dissociation constant of the oxide K_{MO}) is shown in Figs. 2 and 3. The form of the isotherms obtained is typical of adsorption isotherms[38]. It may therefore be assumed that they correspond to processes taking place chiefly on the surface of the crystals and approaching saturation in the region of the inflection on the isotherms. To determine separately the quantities of excess metal located on the surface and

dissolved in the bulk of the crystals, the non-stoichiometric specimens, before the determination of the excess metal, were treated with oxygen at room temperature to remove the excess of metal on the surface without influencing that dissolved in the bulk. As in other experiments[10,31,32], these studies showed that not less than 90% of the excess metal is in fact located on the surface of the crystals, and only about 10% is dissolved in the bulk.

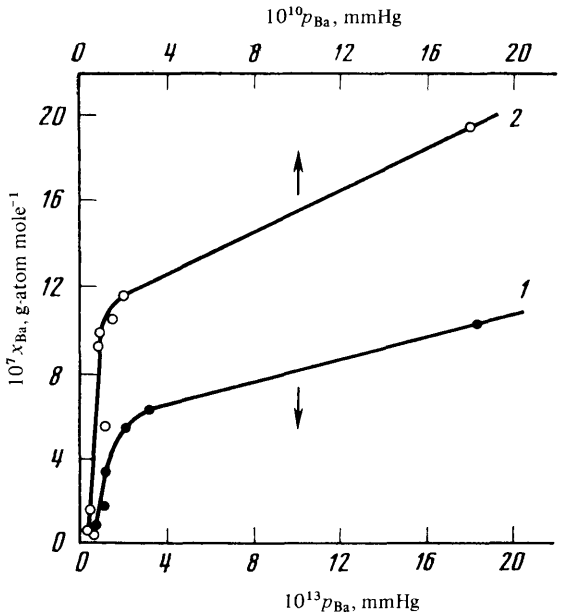


Figure 2. Dependence of the concentration of excess Ba in BaO on the vapour pressure of Ba [36] at 1000° (*1*) and 1150° (*2*).

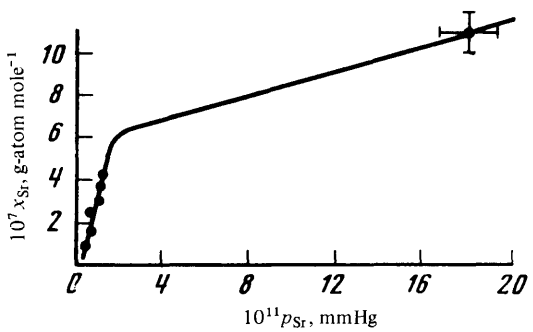


Figure 3. Dependence of the concentration of excess Sr in SrO on the vapour pressure of Sr [37] at 1150°.

At higher M vapour pressures, when the total concentration of excess metal increases chiefly as a result of its dissolution in the bulk, the proportion of excess M due to adsorption on the surface relative to the total concentration of M in the specimen was found to be small. This was confirmed experimentally[39] in a study of the distribution of Ba between the vapour phase and powdered BaO at 1200° in the Ba vapour pressure range 3×10^{-5}–35 mmHg. BaO was saturated with barium using a stream of metal vapour, carried over BaO using helium. The results of the measurements are given in Fig. 1. The experimental points on coordinates $\lg x_{Ba}-\lg p_{Ba}$ are described by two straight lines intersecting at a pressure of ~1 mmHg. In the vapour pressure range 3×10^{-5}–1 mmHg, the equation for the isothermal relationship obtained has the form:

$$x_{Ba} = 7{,}51\cdot10^{-5}p_{Ba}^{0{,}328}, \quad (1)$$

and in the pressure range 1–32 mmHg:

$$x_{Ba} = 1{,}17\cdot10^{-4}p_{Ba}^{1{,}075} \quad (2)$$

(here and subsequently, the solubility is given in g-atom Ba per mole of BaO, and the pressure in mmHg).

In the vapour pressure range 10^{-5}–1 mmHg, the data obtained for powdered specimens[39] show good agreement with the results obtained using single crystals[6,29], indicating that in the pressure range studied, most of the excess Ba is in the bulk of the BaO crystals, and the quantity on the surface is comparatively small. Extrapolation of the data[39] on the solubility of barium in BaO to lower pressures, 10^{-10}–10^{-8} mmHg, shows satisfactory agreement with the data previously obtained for this range[36,37]. In fact, calculation of the concentration of excess barium using Eqn. (1) gives for a pressure of 10^{-9} mmHg the value 0.9×10^{-7} g-atom Ba per mole of BaO, which is about 6% of the total obtained under these conditions in earlier work[36,37] (Fig. 2), and which corresponds approximately to the concentration of excess barium in BaO crystals, remaining in the dissolved state after the surface is cleaned using oxygen. The data[39] for the pressure range above 1 mmHg are close to those obtained earlier[40], but are apparently more accurate, since they were obtained by an improved procedure. The dependence of the solubility on p_{Ba} in this range is the same as for Sr in SrO, [28] Ca in CaO, [27] and Mg in MgO [26] at high metal vapour pressures (see Fig. 1).

2. Excess Oxygen in MO

The most extensive early study of the reaction of BaO with O_2 is that of Hildebrand[41]. In a study of the equilibrium in the BaO–O_2 system in the range 700–800° at oxygen pressures of 10–800 mmHg, Hildebrand found that the solubility isotherms for oxygen in BaO showed two bivariant regions with a univariant region between them, corresponding to equilibrium between two conjugate solid solutions, based on BaO and on BaO_2.

Detailed studies of the solubility of oxygen in BaO and SrO have been carried out in the past ten years in the Mendeleev Moscow Institute of Chemical Technology[42-45]. The equilibria have been studied over a wide range of temperatures and oxygen pressures by a static method in which the quantity of oxygen absorbed by the substance was determined from the decrease in pressure in a known volume.

The solubility of O_2 in BaO was studied at 683–798° and high oxygen pressures (10–500 mmHg).[42] Like Hildebrand[41], the authors cited[42] observed a change in the number of thermodynamic degrees of freedom of the BaO–O_2 system with increase in p_{O_2} under isothermal

conditions (Fig. 4). It was assumed[42] that in the bivariant equilibrium ranges there is one phase in the solid state, interpreted as either a solution of BaO_2 in BaO (first bivariant range) or a solution of BaO in BaO_2 (second bivariant range). For the investigation of the conditions of formation of non-stoichiometric BaO crystals containing excess oxygen, the first bivariant region (I in Fig. 4) is of greatest interest. Under these conditions, the solubility isotherms were described by equations of the form

$$x_O = K_O p_{O_2}^{1/n}; \quad n = 0.88 \div 1.03. \tag{3}$$

The solubility of oxygen in BaO varied in the range 4×10^{-3}–6×10^{-2} mmHg, depending on the conditions of the experiment. Treatment of the data[42] on the solubility of oxygen in BaO in region I (Fig. 4) made it possible to describe them by the analytical equation

$$x_O = 6.6 \cdot 10^{-8} p_{O_2}^{1.0} \exp(+1.61 \cdot 10^4/RT). \tag{4}$$

The temperature coefficient of Eqn. (4) shows that an exothermic chemical reaction takes place when oxygen dissolves in BaO under the above conditions. Thus with increase in temperature the concentration of dissolved oxygen decreases.

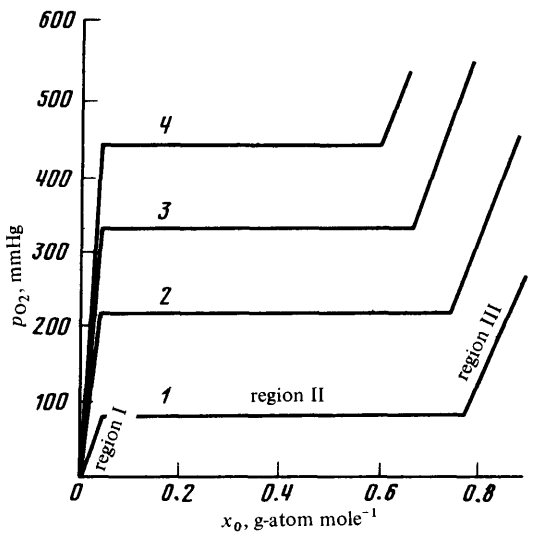


Figure 4. Solubility isotherms for oxygen in BaO [42] at 683° (*1*), 748° (*2*), 773° (*3*), and 790° (*4*).

In the range of the univariant equilibrium (region II in Fig. 4), the temperature dependence of the equilibrium pressure of oxygen above the product of the reaction of BaO with O_2 is given by the equation

$$\lg p_{O_2} = -7500/T + 9.705. \tag{5}$$

The heat of the chemical reaction by which BaO_2 is formed,

$$BaO + 1/2\,O_2 = BaO_2, \tag{6}$$

calculated from the compositions of the conjugate solid solutions and the oxygen pressure in the univariant range, was 18.8 kcal mole^{-1}, in agreement with the value 19.1 kcal mole^{-1}, obtained later[46].

A procedure basically similar to that described above was used to obtain the isothermal dependence of the solubility of O_2 in BaO at 950° and 1150° in the range $p_{O_2} = 2\times10^{-5}$–5 mmHg (Fig. 5).[43] For the oxygen pressure range 5×10^{-4}–5 mmHg, in which the accuracy of the measurements was ±10%, the solubility isotherms were given by the following equations

$$x_O = 1.88 \cdot 10^{-3} p_{O_2}^{1/1.97} \text{ (at 950°)} \tag{7}$$

$$x_O = 9.8 \cdot 10^{-4} p_{O_2}^{1/2.09} \text{ (at 1150°)}. \tag{8}$$

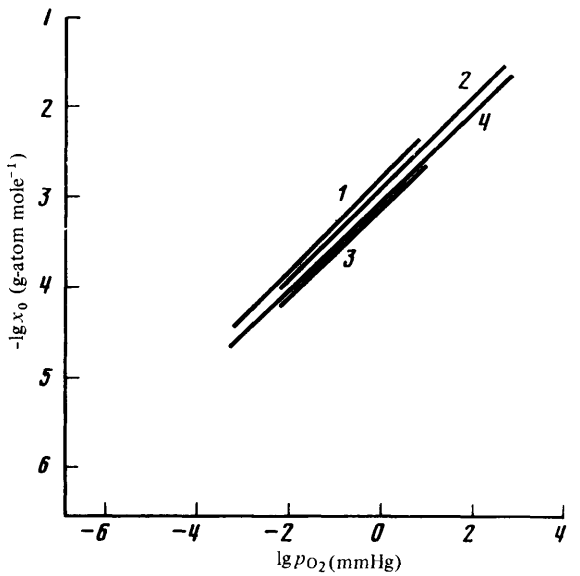


Figure 5. Solubility isotherms for oxygen in BaO at 950° (*1*—from Ref. 43, *2*—from Ref. 47) and at 1150° (*3*—from Ref. 43, *4*—from Ref. 47).

In a later analogous study[47], the solubility of oxygen in BaO was measured at 850–1420° and $p_{O_2} = 5\times10^{-3}$–600 mmHg. The concentration of O_2 absorbed by the oxide was determined by thermogravimetric analysis (TGA) and from the quantity of oxygen liberated when the specimen was dissolved completely in water. The results obtained by these two methods did not coincide, the solubility values obtained from the thermogravimetric measurements being 2–2.5 times those obtained from the gas-volumetric measurements. The former appear more reliable, since in the determination of O_2 by the second method, loss of oxygen as a result of the simultaneous freezing of O_2 and water in the trap cooled by liquid nitrogen is possible. The results obtained by TGA are given in Fig. 6, and are described analytically by the equation

$$x_O = 2.71 \cdot 10^{-5} p_{O_2}^{1/2} \exp(+9080/RT). \tag{9}$$

To measure the bulk absorption of O_2 and its adsorption separately, finely dispersed and coarsely crystalline BaO powders were used[47]. The results of the measurements in the two cases did not differ greatly, indicating that

adsorption makes a relatively small contribution to the measured value of the absorption under the conditions of the experiment.

Comparison shows that these results[43,47] are in agreement (Fig. 5). It should be noted, however, that at $x_O > 2\times10^{-2}$ g-atom O per mole of BaO, the isotherms obtained in one case[47] become steeper (Fig. 6). This apparently indicates that with increase in the concentration of oxygen dissolved in BaO, the law governing the distribution of oxygen between the gaseous phase and the BaO crystals changes.

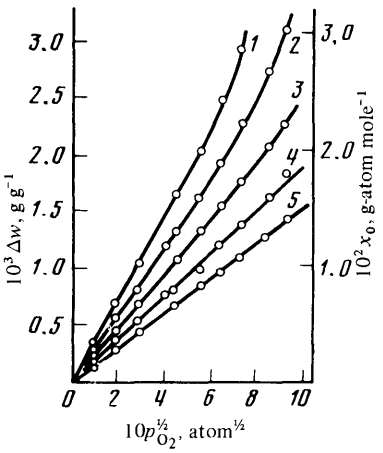


Figure 6. Dependence of the change in weight (Δw) of BaO specimens on the oxygen pressure at 857° (*1*), 927° (*2*), 1027° (*3*), 1127° (*4*), and 1227° (*5*).[47]

Table 1. Coefficients K_O and n in Eqn. (3).[45]

T, °C	700	800	950	1150
10^4K_O	2.77	1.71	1.23	0.93
n	2.37	2.61	2.63	2.66

The SrO–O_2 system was studied in detail at temperatures up to 600° in the range of oxygen pressures 1–100 atm.[48] A range of existence of bivariant equilibria similar to those found in the BaO–O_2 system could not be detected[48]; the stability of SrO_2 was found to be much lower than that of BaO_2.

The solubility of O_2 in SrO was studied[44,45] at 700–1150° and $p_{O_2} = 1\times10^{-5}$–5 mmHg by the method used for BaO.[42,43] The experimental points on coordinates $\lg x_O - \lg p_{O_2}$ were given by straight lines, within the limits of their scatter. The coefficients K_O and n in Eqn. (3), describing the experimental data, are given in Table 1.

Comparison of the solubility of oxygen in SrO and BaO shows that it is lower by approximately an order of magnitude in SrO. As in the case of BaO, however, the solubility of oxygen decreases with increase in temperature.

The data on the solubility of oxygen in MgO [49,50] and CaO [50] are fragmentary and qualitative in character, and give no additional information on the behaviour of excess oxygen in MO.

3. Summary of Data on the Non-stoichiometry of BaO and SrO Specimens Having a Highly Developed Surface

The production of excess M or O in MO both in the bulk of the crystals and on their surface is the factor responsible for the sharp change in the electrophysical properties of the oxides. Thus to select conditions for the synthesis of a substance with required properties, it is necessary to know how the magnitude of the excess of a given component of the compound depends on the vapour pressure and temperature. One method of summarising this relationship is by constructing $p-T-x$ diagrams.

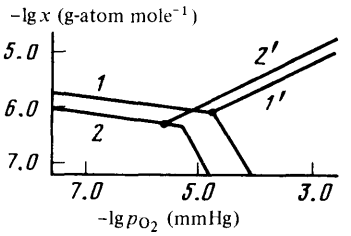


Figure 7. Dependence of the excess component in BaO on p_{O_2}:[51] *1*,*2*) concentration of excess Ba at 1150° and 1000° respectively; *1'*,*2'*) concentration of excess oxygen at 1150° and 950° respectively.

The first attempt to use the results of direct determinations of the excess of the components in BaO to construct this diagram was made by one of the present authors[51]. For this purpose, use was made of the results of measurements using powdered specimens, which are of particular interest since they are used as electron-emitting coatings in thermocathodes. Since in the production of the emitting power of these cathodes, in addition to the excess metal dissolved in the bulk of the crystals, an exceptional role is played by the excess metal localised on their surface, the coordinate reflecting the excess metal in the $p-T-x$ diagram included both the metal dissolved in the bulk of the crystals and the metal situated on the surface. This gave these diagrams the maximum utility for practical applications.

Fig. 7 shows the change in the magnitude of the excess of a component in BaO on p_{O_2} at a given temperature. Lines *1* and *2* show the magnitude of the excess Ba at 1150° and 950°, and lines *1'* and *2'* the excess oxygen at the same temperatures. Taking sections of the isotherms in Fig. 7 along the concentration axis and transferring them to coordinates $\lg p_{O_2} - 1/T$ gave the part of the $p-T-x$ diagram for the pressure range of greatest practical interest[51] (Fig. 8).

The $p-T-x$ diagram for strontium oxide (Fig. 9) was constructed similarly[45], again for specimens having a highly developed surface and for the range of small departures from stoichiometry.

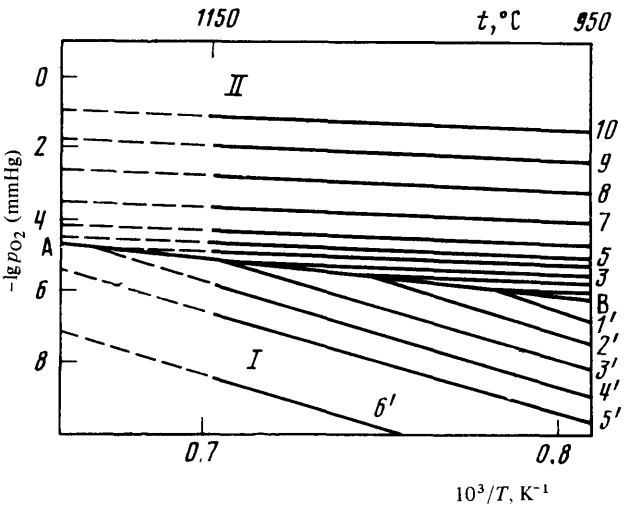


Figure 8. $p-T-x$ diagram for BaO [51] (region *I*—range of excess Ba, region *II*—range of excess oxygen). Concentration of excess components: *1*) 1.8×10^{-6}; *2*) 1.6×10^{-6}; *3*) 1.3×10^{-6}; *4*) 1.0×10^{-6}; *5*) 9.1×10^{-7}; *6*) 7.9×10^{-7}; *7*) 6.3×10^{-7}; *8*) 5.2×10^{-7}; *9*) 2.5×10^{-7}; *10*) 4.0×10^{-6}; *11*) 1.0×10^{-5}.

1. Analysis of Crystal–Vapour Equilibrium

It is of interest to determine the conditions of the crystal–vapour phase equilibrium under which: 1) the overall compositions of the vapour phase and the crystal are the same, and 2) the crystal has the stoichiometric composition.

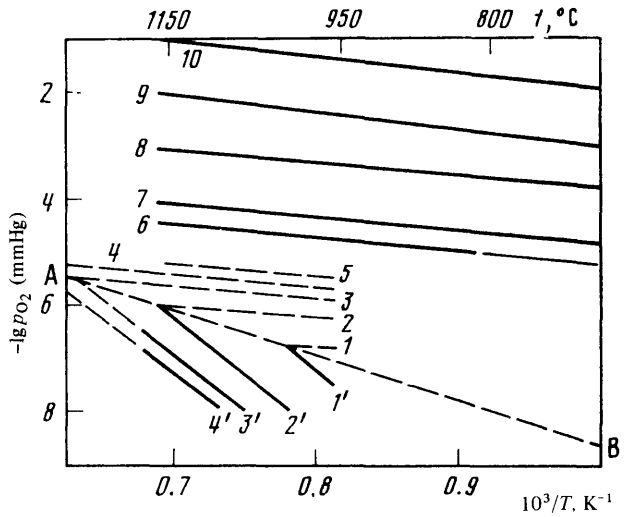


Figure 9. $p-T-x$ diagram for SrO [45] (excess oxygen above line AB, excess strontium below it). Concentration of excess components: *1*) 3×10^{-7}; *2*) 5×10^{-7}; *3*) 6.5×10^{-7}; *4*) 8×10^{-7}; *5*) 1×10^{-6}; *6*) 2×10^{-6}; *7*) 3×10^{-6}; *8*) 7×10^{-6}; *9*) 1.8×10^{-5}; *10*) 4.5×10^{-5}.

III. SOME THERMODYNAMIC PROPERTIES OF MO CRYSTALS

To investigate the nature of the non-stoichiometry of MO crystals, it is useful to draw on experience gained in the thermodynamics of solutions. Thermodynamics makes it possible to regard non-stoichiometric crystals as solid solutions in which the solvent is the main material MO, and the solutes are the excess components, the products of the dissociation of the main substance.

In the thermodynamic analysis of the properties of a non-stoichiometric phase, it is necessary to bear in mind that published data on the departures from stoichiometry do not always contain the required information on the surface area of the specimens studied. This makes it difficult to use these data, since in specimens having a highly developed surface, the magnitude of the departure from stoichiometry is determined not only by pressure and temperature but also by the degree of dispersion of the specimen. Thus the present authors selected from the available experimental data those characterising the excess of the components only in the bulk of the MO crystals, and used the methods of the thermodynamics of solutions in an attempt to analyse various thermodynamic properties of non-stoichiometric crystals and summarise the information in the form of $p-T-x$ diagrams.

With isothermal equilibrium change in the composition of an MO crystal, the vapour pressure above the specimen passes through an extremal value. At the extremal point, the overall compositions of the equilibrium vapour and solid phases are the same, so that volatilisation of the MO crystals at a given temperature can take place without change in the composition of the specimen. The relationship between the concentration of the excess components in MO crystals and the composition of the vapour at the extremal point can be examined.

MO is partly dissociated in the vapour phase. The volatilisation and dissociation of the oxide can be described as follows:

$$\mathrm{MO(solid)} \rightarrow \mathrm{MO(vapour)}, \quad K_{10} = p_{MO}/x_{MO}; \tag{10}$$

$$2\mathrm{MO(vapour)} \rightarrow 2\mathrm{M(vapour)} + \mathrm{O_2}; \quad K_{11} = (p_M^2 p_{O_2})/p_{MO}^2, \tag{11}$$

where x_{MO} is the mole fraction in the solid phase, and K_{10} and K_{11} the equilibrium constants of the corresponding reactions.

The total vapour pressure over the MO crystals is given by the sum

$$p = p_{MO} + p_M + p_{O_2}. \tag{12}$$

To find the vapour pressure extremal point, p_{MO} and p_{O_2} in Eqn. (12) are replaced by p_M, K_{10}, and K_{11}, and the right-hand side of the equation is differentiated with

respect to p_M. The expression obtained is put equal to zero, and transformed to give

$$2p_{O_2}/p_M = 1 + (K_{10} + 2p_{O_2}/x_{MO})\frac{\partial x_{MO}}{\partial p_M}. \quad (13)$$

When the excess components dissolve in MO, processes take place leading to the production of defects of various kinds in the crystal. These processes can be represented in general form as follows:

$$A_{vap} \rightleftarrows (iC + jD + \ldots + rE)_{cryst}, \quad (14)$$

where A represents the metal or oxygen (O_2) in the vapour phase, and C, D, ... E are the new components of the crystal, formed in its interaction with the vapour A.

At the comparatively small departure from stoichiometry observed in alkaline earth metal oxides, their phases can be regarded as very dilute solutions. In this case the equilibrium constant of reaction (14) has the form

$$K = \frac{[C]^i [D]^j \ldots [E]^r}{p_A}. \quad (15)$$

Since

$$[C] = \frac{i}{j}[D] = \ldots = \frac{i}{r}[E], \quad (16)$$

Eqn. (15) can be solved for [C]:

$$[C] = K' p_A^{1/(i+j+\ldots+r)}, \quad (17)$$

where

$$K' = \left[K\left(\frac{i}{j}\right)^j \ldots \left(\frac{i}{r}\right)^r\right]^{1/(i+j+\ldots+r)}$$

Thus the distribution of the excess components between the vapour phase and MO crystals is described in general form by the equations:

$$x_M = K_M p_M^{1/m}, \quad (18)$$

$$x_O = K_O p_{O_2}^{1/n}, \quad (19)$$

where m or n are equal to the sum of the stoichiometric coefficients in the right-hand side of Eqn. (14), or, put differently, are equal to the number of particles and quasi-particles formed in the solid phase from one metal atom or oxygen molecule on going from the vapour to the solid phase. If the particles and quasi-particles formed are regarded as independent chemical components, Eqns. (14) and (15) give the following equation, which is always applicable for a solid solution of the excess components in MO†:

$$x_{MO} + mx_M + \frac{n}{2}x_O = 1. \quad (20)$$

x_{MO} in Eqn. (13) is expressed in terms of x_M and x_O, using Eqn. (20). x_M and x_O are then replaced by their values from Eqns. (18) and (19). Since x_M and x_O are much smaller than 1, this gives the approximate equation

$$2p_{O_2} = p_M - K_{10}\delta, \quad (21)$$

where $\delta = x_M - x_O$. When the homogeneity range of the compound is extremely narrow, that is $\delta = 0$, it follows that at the point of minimum vapour pressure

$$2p_{O_2} = p_M. \quad (22)$$

From published data on the dissociation constant of MO

$$K_{MO} = K_{10}^2 K_{11} = p_M^2 p_{O_2}/x_{MO}, \quad (23)$$

where $x_{MO} \simeq 1$, it is possible to calculate p_M at the vapour pressure extremal point with allowance for Eqn. (22). At the total vapour pressure minimum

$$p_M = (2K_{MO})^{1/3}. \quad (24)$$

Eqns. (18), (19), and (22) can be used to find the vapour pressure of M over MO crystals having the stoichiometric composition at $\delta = 0$, and also the concentration of quasi-excess M and O at this point. For this purpose, Eqns. (18) and (19) are equated, and in Eqn. (19) p_{O_2} is expressed in terms of p_M, using Eqn. (23). This gives:

$$p_M = \left(\frac{K_O K_{MO}^{1/n}}{K_M}\right)^{mn/(n+2m)}. \quad (25)$$

The value of p_M at $\delta = 0$ is substituted in Eqn. (18) to obtain the concentration of quasi-excess components:

$$x_M = x_O = (K_{MO} K_O^n K_M^{2m})^{1/(n+2m)}. \quad (26)$$

The total concentrations of both quasi-excess components in the stoichiometric crystal are obviously equal to $2x_M$.

It is possible to calculate p_M at the total vapour pressure minimum, and also p_M and x_M at $\delta = 0$ for BaO. The dissociation constant of BaO is known[52]:

$$\lg K_{BaO} = -\frac{352.1 \cdot 10^3}{4.57T} + 40.54 - 3.6 \lg T, \ (\text{mmHg})^3 \quad (27)$$

Eqns. (24) and (27) are used to find p_{Ba} at the total vapour pressure minimum

$$\lg p_{Ba} = \lg(2p_{O_2}) = -\frac{117.4 \cdot 10^3}{4.57T} + 13.82 - 1.20 \lg T. \quad (28)$$

To calculate p_{Ba} and x_{Ba} at $\delta = 0$, it is necessary to know not only K_{BaO} but also K_O, K_{Ba}, m, and n. The values of K_O and n are known from Eqn. (9). The solubility of excess Ba in BaO for an infinitely dilute solution is given in general form by the equation

$$x_{Ba} = C p_{Ba}^{1/m} \exp(-A/RT), \quad (29)$$

where A, C, and m are constants. From published data, the parameter $m = 3$ [9,14,22] and $A = 5$–10 kcal mole^{-1}; [29] in the present work it was assumed that $A = 7.0$ kcal mole^{-1}, and the apparently most reliable data[14] then gave

$$x_{Ba} = 8 \cdot 10^{-4} p_{Ba}^{1/3} \exp(-7 \cdot 10^3/RT). \quad (30)$$

p_{Ba} and x_{Ba} are now obtained for $\delta = 0$:

$$\lg p_{Ba} = -\frac{120.0 \cdot 10^3}{4.57T} + 14.10 - 1.35 \lg T; \quad (31)$$

$$\lg x_{Ba} = \lg x_O = -\frac{47.0 \cdot 10^3}{4.57T} + 1.61 - 0.45 \lg T. \quad (32)$$

Comparison of Eqns. (28) and (31) shows that for BaO, the composition of the crystal at the extremal vapour pressure will differ only slightly from the stoichiometric composition, particularly at temperatures above 1000°. The value of x_{Ba} is calculated assuming that $\delta = 0$ at $p_{Ba} = 2p_{O_2}$. For this purpose, the value of p_M from Eqn. (24) is substituted in Eqn. (25):

$$K_M = 2^{-1/3} K_O (K_{MO}/4)^{1/18}. \quad (33)$$

† In the general case, the coefficients of x_M and x_O are equal to

$$\left(\frac{i+j+\ldots+r}{i}\right),$$

where $i = 1$ or 2 for the dissolution of a metal atom or an oxygen molecule respectively.

Thus

$$x_{Ba} = 1.0 \cdot 10^{-3} p_{Ba}^{1/3} \exp(-10.5 \cdot 10^3/RT). \quad (34)$$

At high temperatures, Eqn. (34) gives values of x_{Ba} close to those obtained from Eqn. (30).

Similar calculations can be carried out for strontium oxide. The expression for the dissociation constant of SrO [52] is:

$$\lg K_{SrO} = -\frac{362.0 \cdot 10^3}{4.57T} + 40.40 - 3.27 \lg T \ (\text{mmHg})^3. \quad (35)$$

The extremal vapour pressure of SrO corresponds to the following value of p_{Sr}, calculated from Eqns. (24) and (35):

$$\lg p_{Sr} = \lg(2p_{O_2}) = -\frac{120.1 \cdot 10^3}{4.57T} + 13.75 - 1.09 \lg T. \quad (36)$$

To calculate p_{Sr} and x_{Sr} at $\delta = 0$, the experimental dependence of x_O on p_{O_2}, which is more complex than that for BaO, is first analysed, The parameter n in Eqn. (19) is fractional (see Table 1), apparently indicating that oxygen is distributed by two competing mechanisms[45]. Since n is close to 2, it appears natural to assume that one of the mechanisms, probably the principal mechanism, is described by a distribution law which is similar to that for BaO and has the parameter $n = 2$. Thus the relationship between the concentration of excess oxygen in SrO and the oxygen pressure is represented in the form of the sum:

$$x_O = K_1 p_{O_2}^{1/2} + K_2 p_{O_2}^{1/f}, \quad (37)$$

where the first term on the right-hand side of the equation corresponds to the principal distribution law.

Table 2. Coefficients K_1 and K_2 in Eqn. (34).

T, °C	700	800	950	1150
$10^4 K_1$	2.6	1.9	1.2	0.64
$10^5 K_2$	2.4	3.1	2.3	2.7

Eqn. (37) gives the best description of the experimental data (practically within the range of scatter) if it is assumed that $f = 4$ (for $f = 3$, 5, or 6 greater deviations from the interpolation line are obtained). The calculated coefficients K_1 and K_2 are given in Table 2. The second mechanism makes a practically constant contribution to the value of x_O at a fixed p_{O_2}, irrespective of temperature in the range 700–1150°C. This is possible if it is assumed that the additional absorption is background absorption. The temperature dependence of the solubility of oxygen in SrO for the principal mechanism is described by the equation

$$x_O = 4.0 \cdot 10^{-6} p_{O_2}^{1/2} \exp(+9.0 \cdot 10^3/RT). \quad (38)$$

When K_O and K_{SrO} are known, it is possible to find x_{Sr} from Eqn. (33):

$$x_{Sr} = 1.4 \cdot 10^{-4} p_{Sr}^{1/3} \exp(-11 \cdot 10^3/RT), \quad (39)$$

assuming that, as in the base of BaO, $m = 3$.

At the point $\delta = 0$, the concentration of quasi-excess Sr is given by

$$\lg x_{Sr} = \lg x_O = -\frac{52.2 \cdot 10^3}{4.57T} + 1.08 - 0.41 \lg T. \quad (40)$$

Fig. 10 gives the calculated solubility isotherms for the excess Sr and oxygen in SrO at 1150°, together with experimental data[45] on the solubility of oxygen in SrO and data[28] on the solubility of Sr in SrO at high metal vapour pressures. The calculated isotherms show satisfactory agreement with the experimental isotherms obtained for other vapour pressure ranges.

2. Properties of the Solid Solution of M in MO Close to the Solidus Line

At high metal vapour pressures close to the solidus line, the concentration of excess M in MO is proportional to p_M (see Fig. 1), that is the distribution of M between the vapour and solid phases is described by Henry's law: $x_M \sim p_M$. The influence of temperature on the solubility of M in MO in this range of values of p_M can be examined. For the qualitative discussion of this question, the approximation of regular solutions can be used. In this case the activity coefficient (γ_M) is given by the equation[53]:

$$\lg \gamma_M = \alpha/RT, \quad (41)$$

where α is a constant parameter which has the significance of the differential molar heat of solution. The activity of M in the solid solution is given by the expression

$$a_M = \gamma_M x_M = p_M/(p_M^0)_{\text{solid}}, \quad (42)$$

where p_M is the vapour pressure of M above the solution of M in MO, and $(p_M^0)_{\text{solid}}$ the vapour pressure of the pure solid metal.

Substituting Eqn. (41) in Eqn. (42) gives

$$\ln x_M = -\alpha/RT + \ln[p_M/(p_M^0)_{\text{solid}}]. \quad (43)$$

The value of α calculated using data on the solubility of M in MO, given in Fig. 1, and on the saturated vapour pressure of the solid alkaline earth metals[7,25,54]. For BaO, SrO, CaO, and MgO, the calculated values of the parameter α are 14.1, 18, 19, and 33 kcal mole^{-1} respectively. Analysis of Eqn. (43) shows that if the heat of sublimation of M is greater than α, the solubility of M in MO at a given vapour pressure decreases with increase in temperature. Comparison of the values of α with the heats of sublimation, equal to 42, 36, 41, and 34 kcal mole^{-1} for Ba, [7] Sr, Ca, and Mg [54] respectively, shows that the solubility should decrease with increase in temperature for BaO, SrO, and CaO. This is confirmed by available experimental data for SrO [28] (see Fig. 1). The solubility of atoms of the alkali metals in crystals of their halides shows a similar temperature dependence[55]. For a solution of Mg in MgO, the values of the heat of sublimation and α coincide. The temperature dependence of the solubility in this case is determined by the deviations of the properties of the real solution from those of a regular solution. The solubility of Mg in MgO increases with temperature (see Fig. 1), [26] in contrast to the oxides of the other alkaline earth metals.

Fig. 11 gives the solubility isotherms for Ba in BaO, calculated from Eqn. (30) at low Ba vapour pressures and from Eqn. (43) at high pressures. In Eqn. (43) the vapour pressure over solid Ba was calculated from the equation[7]:

$$\lg(p_{Ba}^0)_{\text{solid}} = 8.34 - (9.2 \cdot 10^3/T). \quad (44)$$

Fig. 11 shows that the isotherms intersect. At the points of intersection, however, the compositions of the solid solutions, which are at different temperatures, are not the same. At a higher temperature, the excess Ba in

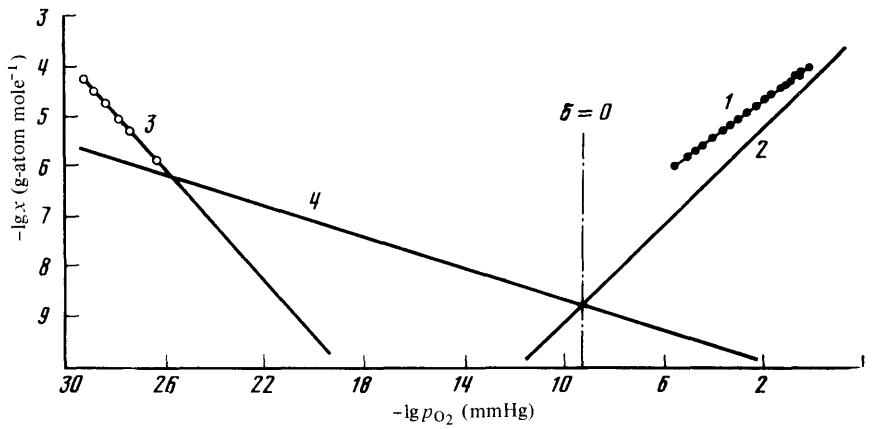


Figure 10. Solubility isotherms for excess strontium and oxygen in SrO at 1150°: *1*) oxygen solubility isotherm[45]; *2*) solubility isotherm for oxygen in the form of the complexes (O_2^{2-})(solid), calculated from Eqn. (35); *3*) Sr solubility isotherm[28], corresponding to the formation of $V_O^{\times}$; *4*) solubility isotherm for Sr in SrO, calculated from Eqn. (36) and corresponding to the formation of defects of the type $V_O^{\cdot\cdot}$ in SrO.

the solution predominates in a form corresponding to the distribution law: $x_{Ba} \sim p_{Ba}^{1/3}$. The points of intersection evidently correspond to identical total concentrations of excess Ba, which is however present in different states in BaO. A similar phenomenon should be observed for solutions of the excess metals in SrO and CaO.

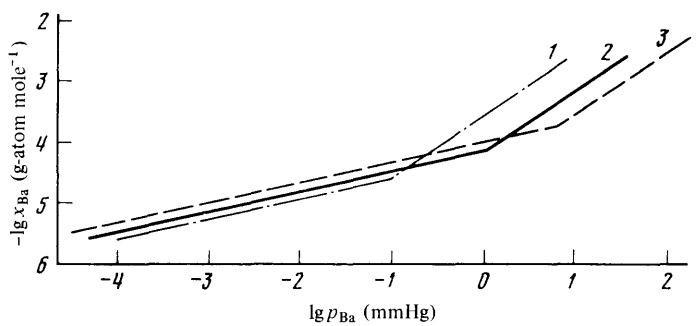


Figure 11. Solubility isotherms for Ba in BaO, calculated from Eqns. (27) and (40) for 1000° (*1*), 1200° (*2*), and 1400° (*3*).

The above discussion dealt only with the change in the properties of the solute—the excess metal—with change in the vapour pressure of M. The analysis of the behaviour of the solvent with increase in the concentration of excess metal in the solution is also of undoubted interest. The Gibbs–Duhem equation is used, with the assumption that at high vapour pressures of M, the system can be regarded as a two-component system consisting of M and MO. At a constant temperature, the Gibbs–Duhem equation has the form

$$dp = c_M d\mu_M + c_{MO} d\mu_{MO}, \qquad (45)$$

where p is the total pressure above the phases; $c_i = n_i/V$ (n is the number of moles of the component in the phase, and V the volume of the phase); and μ_i the chemical potential of the component. In the range of vapour pressure in which the solubility of M in MO obeys Henry's law, the vapour pressure of MO is smaller than p_M by many orders of magnitude[26-29,39,52]. It may therefore be assumed that $p = p_M$. Since the chemical potentials of a given component in the equilibrium phases are the same, $\mu_M = \mu_M^{vapour}$ (μ_M^{vapour} is the chemical potential of M in the vapour phase). Since the vapour phase is ideal,

$$d\mu_M^{vapour} = RT\, d\ln p_M = d\, p_M/c_M^{vapour}, \qquad (46)$$

where $c_M^{vapour} = n^{vapour}/V^{vapour}$ is the molar concentration of M in the vapour phase. Substituting Eqn. (46) in Eqn. (45) gives

$$d\mu_{MO} = \left(\frac{1-\beta}{c_{MO}}\right) p_M, \qquad (47)$$

where $\beta = c_M/c_M^{vapour}$ is a function of temperature alone, as follows from Henry's law.

Integration of Eqn. (47) gives the change in the chemical potential of the solvent with increase in p_M:

$$\Delta\mu_{MO} = \left(\frac{1-\beta}{c_{MO}}\right)\Delta p_M. \qquad (48)$$

This equation (for the change in the quantity p_{MO}) was first derived by Gibbs[56]. From the equation it follows that for $\beta < 1$, the chemical potential of MO, and hence p_{MO}, increase with increase in p_M and the concentration of excess M in MO; for $\beta = 1$, the chemical potential remains unchanged under the same conditions; and finally it decreases for $\beta > 1$. From data on the solubility of M in MO it follows that for solutions of Ba in BaO, Sr in SrO, and Ca in CaO, the parameter $\beta > 1$, so that the chemical potential of MO decreases with increase in the concentration of excess metal in the crystal. On the other hand, in the case of a solution of Mg in MgO, the parameter $\beta < 1$, and the chemical potential of MgO increases.

Thus the thermodynamic properties of a solution of excess Mg in MgO differ from the properties of solutions of the excess metal in the oxides of the other alkaline earth metals. This is quite regular, since the other physicochemical properties of magnesium oxide differ significantly from the properties of the other oxides of this homologous series[57].

3. Range of Existence of BaO on the $T-x$ Diagram

Measurements of the solubility of oxygen in BaO, carried out at low temperatures[42] (Fig. 4), give the position of the solidus line bounding the range of existence of BaO on the BaO_2 side. Fig. 12 shows that the range of existence of BaO increases with temperature, apparently as far as the eutectic temperature (~800° [58]). This part of the solidus line is described analytically by the equation[42]:

$$\lg x_O = -4333/T + 2{,}863. \qquad (49)$$

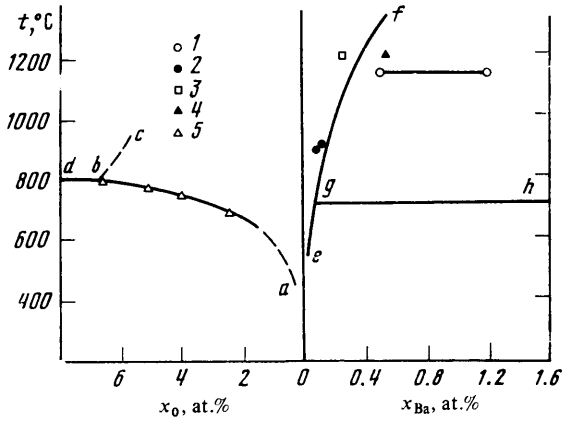


Figure 12. Range of existence of BaO (to the right of the line *abc*, to the left of the line *ef*): *1*) from Ref. 2; *2*) from Refs. 3 and 4; *3*) from Ref. 24; *4*) from Ref. 39; *5*) from Ref. 42; the lines *bd* and *gh* mark the temperatures of the eutectic reactions.

With increase in temperature above the eutectic temperature, a decrease in solubility can be expected, as a consequence of the decrease in the activity of BaO_2 in the melt in equilibrium with the phase BaO.

Several points of the solidus line bounding the range of existence of the phase BaO on the Ba side were obtained by Schriel[2], Kane[3], Libowitz[4], and others[24,35,39,40]. These data are given in Fig. 12. The temperature of the eutectic in the BaO–Ba system is ~710°.[2] Fig. 12 shows that the solubility of Ba in BaO is retrograde. To verify the degree of self-consistency of the published data[2-4,24,25,39,40], the position of the solidus line can be calculated using Eqn. (43), in which α = 14.1 kcal mole^{-1}, and $(p^0_{Ba})_{solid}$ is given by Eqn. (44). The vapour pressure of Ba over BaO crystals in equilibrium with molten Ba [2] should be much lower than the saturated vapour pressure of pure liquid Ba, since BaO is appreciably soluble in liquid Ba. To calculate p_{Ba} it is assumed that the solution of BaO in Ba is ideal. The solubility of BaO in liquid Ba is known[2]. The results of the calculation are given in Table 3. For 1200°, the calculated value of the vapour pressure of Ba, equal to 31 mmHg, is close to the measured value[39,40] (35 mmHg). The solidus calculated from Eqn. (43) is fairly close to the experimental points (Table 3 and Fig. 12).

Table 3. Solubility of Ba in BaO in contact with molten Ba.

T, °C	$(p^0_{Ba})_{liq.}$, mmHg (Ref.25)	Concn. of BaO in molten Ba, mole % (Ref.2)	p_{Ba} from liquidus line, mmHg	$(p^0_{Ba})_{solid}$, mmHg (Ref.24)	Solubility of Ba in BaO, at.%		
					calc.	exp.	refs.
900	2.4	30	1.7	2.8	0.17	0.07—0.12	3, 4
1150	38.1	42	22.0	51.3	0.34	0.5—1.2	2
1200	59.0	48	31.0	81.3	0.39	0.24	40
						0.53	39

Unfortunately, for the oxides of the other alkaline earth metals the data on the homogeneity range are even more fragmentary than for BaO. Comparison of the solubility isotherms for M in MO, given in Fig. 1, merely indicate a tendency for the solubility of M in MO to decrease in the order BaO, SrO, CaO, MgO. The same is true of the solubility of oxygen in MO, as can be seen by comparing its solubility in BaO and SrO (see Part I). Thus the range of existence of MO on the $T-x$ diagram becomes narrower from BaO to MgO.

4. $p-T-x$ Diagram of BaO

The experimental and calculated data on the solubility of the excess components in BaO can be conveniently summarised in the form of the $p-T-x$ diagram, constructed on coordinates $\lg p_{Ba} - 1/T$. This diagram is given in Fig. 13. On these coordinates, the solidus line on the Ba side at low temperatures, when the solubility of BaO in Ba is low, practically coincides with the line giving the temperature dependence of the saturated vapour pressure of pure Ba. In Fig. 13 this is taken from published data[24,25]. At higher temperatures, when the solubility of BaO in molten Ba becomes appreciable, the vapour pressure of Ba, corresponding to the solidus line, becomes lower than the vapour pressure over pure Ba. In this range, the solidus line was constructed from the calculated data given in Table 3. Part of the solidus line (the line *aa*), defining the vapour pressure of Ba in the range of equilibrium of the phases BaO and BaO_2, was constructed using Eqn. (5), which gives the value of p_{O_2} in this range. The value of p_{Ba} was calculated from the known value of p_{O_2} and the dissociation constant of BaO [52] using the equation

$$p_{Ba} = (K_{BaO}/p_{O_2})^{1/3}. \qquad (50)$$

The isoconcentrates on coordinates $\lg p_{Ba} - 1/T$ (Fig. 13) were constructed using Eqns. (4), (9), (30), and (43), describing the solubility of the excess components in BaO in different regions of the diagram. The line *bb* in the diagram is described by Eqn. (28) and corresponds to the

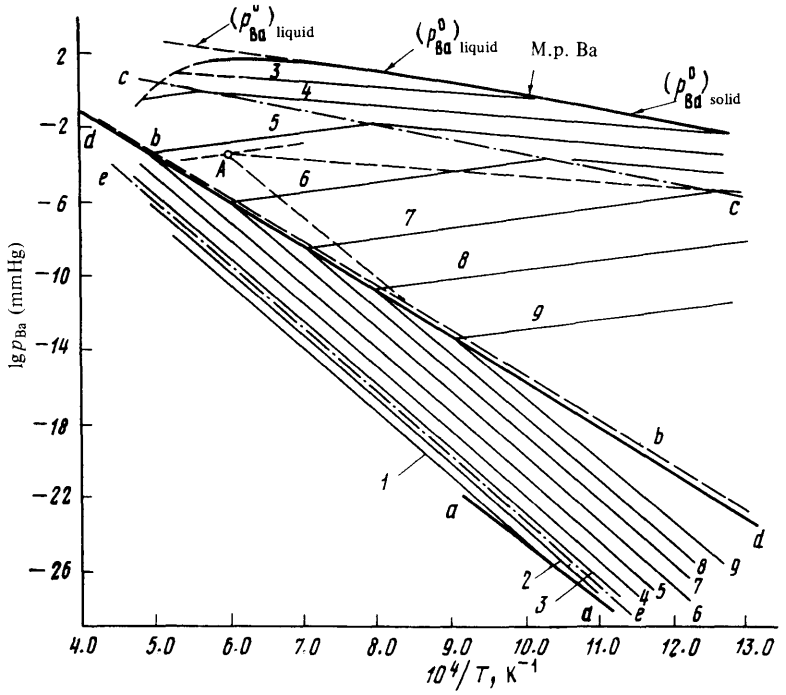


Figure 13. $p-T-x$ diagram for BaO containing excess Ba and oxygen in the bulk of the crystals. The figures at the isoconcentrates give the powers of 10^{-n}, equal to the concentration of the dissolved component.

minimum vapour pressure over BaO crystals. The line *dd* is described by Eqn. (31) and defines the conditions of existence of BaO crystals of stoichiometric composition. The line *cc* gives the change in the distribution law for excess Ba: below this line, $x_{Ba} \sim p_{Ba}^{1/3}$, and above it, $x_{Ba} \sim p_{Ba}$. Its position was calculated from the points of intersection of the isoconcentrates defined by Eqns. (29) and (43).

The isoconcentrates of the excess oxygen are given below the line *dd*. At a concentration of oxygen in BaO greater than $\sim 5 \times 10^{-3}$, the nature of the distribution of oxygen between BaO and the vapour phase changes: the solubility is described by Eqn. (4) at higher concentrations, and by Eqn. (9) at lower concentrations. On coordinates $\lg p_{Ba} - 1/T$, the isoconcentrates described by these equations are parallel to one another. Thus the change in the distribution law takes place fairly smoothly in the concentration range 1×10^{-3}–1×10^{-2}, approximately along the line *ee*.

The isoconcentrates given on the $p-T-x$ diagram (Fig. 13) can obviously be extended beyond the limits of the lines corresponding to the change in the predominant distribution law: *dd*, *cc*, and *ee*. For example, the BaO crystal under the conditions corresponding to point *A* in the diagram contains 8×10^{-6} excess Ba in a form which corresponds to the distribution law (29); 1×10^{-7} excess Ba in a form corresponding to the distribution law (43); 1×10^{-9} excess oxygen in a form corresponding to the distribution law (9), and finally $\sim 10^{-15}$ excess oxygen in a form corresponding to the distribution law (4).

The $p-T-x$ diagram in Fig. 13 can be used to find the conditions for preparing BaO crystals having a given concentration of excess components in a given form. The $p-T-x$ diagram illustrates the mutally unambiguous correspondence between the compositions of the non-stoichiometric crystals under equilibrium conditions and under the conditions of their preparation, completely determined by the vapour pressure of Ba (or O_2) and temperature. In particular, the diagram shows that the fact that the concentrations of an excess component, determined in crystals by chemical methods, are equal cannot be taken as a criterion indicating that the properties of the crystals are identical, since an excess of equal magnitude can be created by an excess component present in different states. The diagram also shows that the form of existence of excess components may change when the crystals are cooled from the temperature of synthesis, when breakdown of the solid solution has not yet taken place.

The $p-T-x$ diagram given in Fig. 13 is to a considerable extent a calculated diagram, and must therefore be regarded as semi-quantitative. To refine it, it is necessary to carry out additional experiments on the direct determination of the concentration of excess components and to study the coefficients of self-diffusion and electrical properties of the crystals under conditions of equilibrium with the vapour phase. A study of the diffusion of barium in BaO at temperatures greater than 1400° indicated that a change in the distribution law for oxygen between the vapour and BaO crystals is possible. The

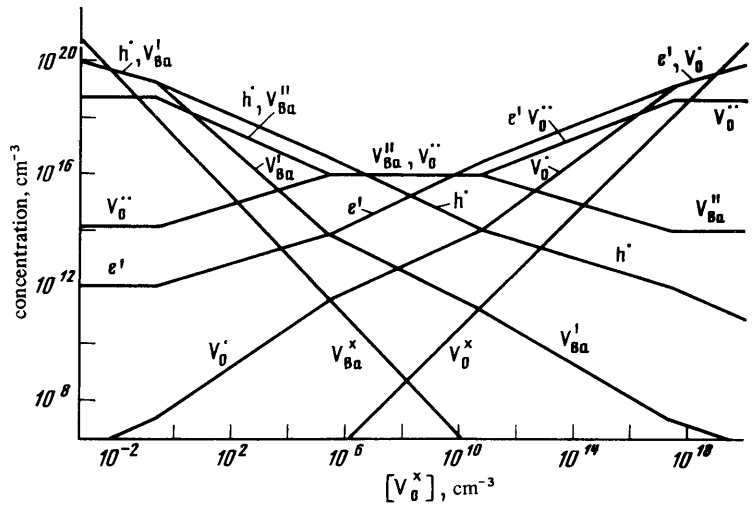


Figure 14. Dependence of the concentration of point defects in BaO on p_{Ba} at 1200° [60] for the case where $K''_S > K_i > K'_S$, where K''_S is the equilibrium constant for the formation of a pair of doubly ionised Ba and O vacancies, K'_S the same for a pair of singly ionised vacancies, and K_i the equilibrium constant for the formation of an "electron–hole" pair.

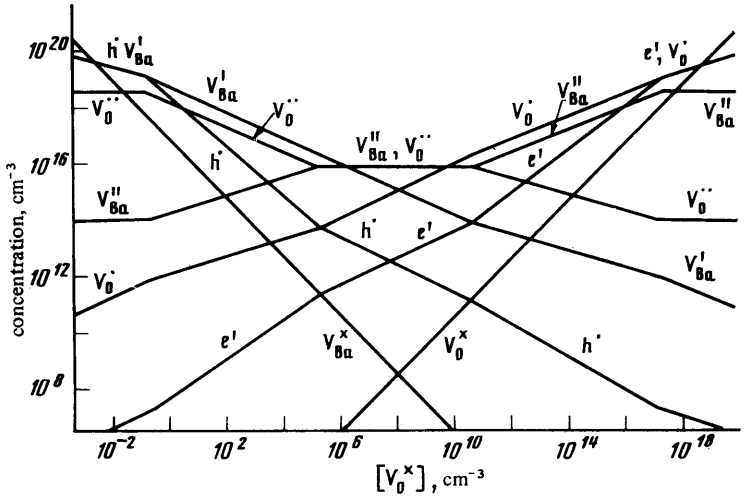


Figure 15. Dependence of the concentration of point defects in BaO on p_{Ba} at 1200° [60] for the case where $K''_S > K'_S > K_i$ (for symbols see caption to Fig. 14).

diffusion coefficient of barium under these conditions became proportional to $p_{O_2}^{1/6}$. The possibility of a change in the nature of the distribution of Ba and O_2 at low temperatures cannot be excluded.

IV. NATURE OF THE INTRINSIC ATOM DEFECTS IN MO

The electrophysical and optical properties of MO, including recent published data, have been reviewed by Kroeger[60], Kofstad[61], and Tret'yakov[62]. Kroeger gave (in the form of diagrams) two possible versions of the equilibrium for the defects in BaO; no refinements were introduced in the later reviews[61,62]. These diagrams are given in Figs. 14 and 15.

Recent papers on the direct quantitative determination of the solubility of M and O in MO give new material from which definite suggestions can be made regarding the nature of the intrinsic atomic defects in MO, and the picture of the equilibrium for defects given by Kroeger[60] can be refined.

1. Defects in BaO

The solubility isotherms for Ba in BaO (Fig. 1) show that Ba atoms dissolved in BaO at low Ba vapour pressures (below 1 mmHg at 1200°) dissociate into several particles. Under these conditions, according to published data[4,5], colour centres having a low rate of diffusion are formed, indicating that the defects produced are vacancies. This is confirmed by data[63] on the concentration of the BaO lattice and the observed[21] absence of any relationship between the absorption spectra of BaO crystals and the nature of the alkaline earth metal dissolved in them. According to Timmer[6] and Kroeger[60], the solution of Ba most probably takes place by the following mechanism:

$$\mathrm{Ba(vapour)} = \mathrm{Ba}_{\mathrm{Ba}}^{\times} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} + 2\mathrm{e}'. \qquad (51)$$

If the condition for electrical neutrality of the crystal has the form

$$2[\mathrm{V}_{\mathrm{O}}^{\cdot\cdot}] = [\mathrm{e}'], \qquad (52)$$

then

$$[\mathrm{V}_{\mathrm{O}}^{\cdot\cdot}] \sim p_{\mathrm{Ba}}^{1/3}, \qquad (53)$$

as observed experimentally[6,39].

At higher Ba vapour pressures (above 1 mmHg at 1200°), the introduction of Ba into BaO takes place without dissociation. In the opinion of some authors[9,24], the excess Ba is situated in interstices:

$$\mathrm{Ba(vapour)} = \mathrm{Ba}_i^{\times}, \quad K_{54} = [\mathrm{Ba}_i^{\times}]/p_{\mathrm{Ba}}, \qquad (54)$$

or a solution of Ba_2O "molecules" in BaO is formed:

$$\mathrm{Ba(vapour)} + \mathrm{BaO} = \mathrm{Ba_2O}, \quad K_{55} = [\mathrm{Ba_2O}]/p_{\mathrm{Ba}}. \qquad (55)$$

The distribution law has the same form in the two cases. It can readily be seen that the nature of the distribution law is preserved if it is assumed that the solution of the excess Ba leads to the production of neutral oxygen vacancies which, like the F-centres in alkali metal halide crystals[60], are colour centres in red BaO crystals:

$$\mathrm{Ba(vapour)} = \mathrm{Ba}_{\mathrm{Ba}}^{\times} + \mathrm{V}_{\mathrm{O}}^{\times}, \quad K_{56} = [\mathrm{V}_{\mathrm{O}}^{\times}]/p_{\mathrm{Ba}}. \qquad (56)$$

Additional information is required before preference can be given to either mechanism.

As in the solution of Ba, several insertion mechanisms are observed in the solution of oxygen in BaO. At comparatively low pressures of oxygen, and hence low concentrations of excess oxygen dissolved in BaO, its concentration is proportional to the square root of the oxygen pressure (see Part II). This law should also be observed when the excess oxygen forms an atomic solid solution, and also when it dissolves in BaO as the peroxide. In the first case the following quasi-chemical reactions of solution are possible in principle[47]:

$$\tfrac{1}{2}\mathrm{O_2} = \mathrm{O}_{\mathrm{O}}^{\times} + \mathrm{V}_{\mathrm{Ba}}^{\times}, \quad K_{57} = [\mathrm{V}_{\mathrm{Ba}}^{\times}]/p_{\mathrm{O_2}}^{1/2}, \qquad (57)$$

$$\tfrac{1}{2}\mathrm{O_2} = \mathrm{O}_i^{\times}, \quad K_{58} = [\mathrm{O}_i^{\times}]/p_{\mathrm{O_2}}^{1/2}. \qquad (58)$$

Since however the heat of dissociation of oxygen molecules to oxygen atoms is large, it is to be expected that the total thermal effect of reaction (57) or (58) will be endothermic, and not exothermic, as found experimentally[43,47]. It was therefore suggested[43] that in the solution of oxygen, the formation of barium peroxide takes place preferentially:

$$\tfrac{1}{2}\mathrm{O_2} + \mathrm{BaO} = \mathrm{BaO_2}, \quad K_{59} = x_{\mathrm{BaO_2}}\gamma_{\mathrm{BaO_2}}/a_{\mathrm{BaO}}p_{\mathrm{O_2}}^{1/2}, \qquad (59)$$

where a_{BaO} is the activity of BaO, equal to ~1, and γ_{BaO_2} the activity coefficient of BaO_2 dissolved in BaO (since the solution of BaO_2 in BaO is dilute, γ_{BaO_2} is constant at a given temperature). The same conclusion was reached in later work[47].

Because of the fundamental importance of this question, the enthalpies of various processes taking place when oxygen is dissolved in BaO with the formation of a solid solution of BaO_2 in BaO will be calculated. Differentiation of the expression for $\ln K_{59}$ obtained from Eqn. (59) with respect to temperature at p_{O_2} = const gives

$$\partial \ln K_{59}/\partial T = \partial \ln \gamma_{\mathrm{BaO_2}}/\partial T + \partial \ln x_{\mathrm{BaO_2}}/\partial T. \qquad (60)$$

If both sides of Eqn. (60) are multiplied by RT^2, the term on the left-hand side of Eqn. (60) acquires the significance of the enthalpy of the reaction (ΔH_r) for BaO_2 formation, and the term $(-RT^2\,\partial \ln \gamma_{BaO_2}/\partial T)$ is the differential molar heat of solution of BaO_2 in BaO ($\Delta\bar{H}_{BaO_2}$). Thus from Eqn. (60) it follows that

$$\Delta H_p = -\Delta\bar{H}_{\mathrm{BaO_2}} + RT^2\partial \ln x_{\mathrm{BaO_2}}/\partial T. \qquad (61)$$

From Eqn. (9), $RT^2\partial \ln x_{BaO_2}/\partial T = -9.1$ kcal mole^{-1}, and the published[42] enthalpy of reaction (59) is −18.8 kcal mole^{-1}. Thus $\Delta\bar{H}_{BaO_2}$ = 9.7 kcal mole^{-1}, and the solution of BaO_2 in BaO is endothermic, as expected from the large positive deviations from ideal behaviour shown by the solution of BaO_2 in BaO. The overall heat of solution of oxygen in BaO is exothermic, however, because of the large exothermicity of reaction (59).

According to Swalin and coworkers[47], reaction (58) indicates that combined pairs of oxygen atoms are formed in the BaO lattice

$$\tfrac{1}{2}\mathrm{O_2} + \mathrm{O}_{(\mathrm{solid})}^{2-} = (\mathrm{O_2^{2-}})_{(\mathrm{solid})} \qquad (62)$$

(O^{2-}(solid) is the anion in the site of the BaO crystal lattice), and these pairs should be arranged along the (100) direction in the BaO crystal lattice. In the opinion of the authors cited[47], the formation of these complexes should lead to expansion of the BaO crystal lattice. Their calculated expansion practically coincides with that found experimentally by X-ray diffraction. The complexes (O_2^{2-})(solid) are apparently analogous to the combined pairs of oxygen ions in the crystal lattice of BaO_2.[64] The two O^{2-} ions in the complex are identical, as a consequence of a slight displacement of the O^{2-} ion in the lattice site when the complex is formed.

The equilibrium constant of reaction (62) has the form

$$K_{62} = [(\mathrm{O_2^{2-}})_{(\mathrm{solid})}]/p_{\mathrm{O_2}}^{1/2}. \qquad (63)$$

Thus $[(O_2^{2-})(\mathrm{solid})] \sim p_{O_2}^{1/2}$, which corresponds to the experimentally observed dependence of the solubility of oxygen on p_{O_2}. Recent measurements[59] of the coefficient of self-diffusion of Ba in BaO at comparatively high pressures of oxygen confirm mechanism (62). At 900–1400°, the coefficient of self-diffusion of Ba is independent of p_{O_2} in the range of pressures studied, 1×10^{-5}–1 atm.[59]

At high concentrations of oxygen in BaO (directly adjacent to the solidus line), the distribution law for oxygen between BaO and the vapour phase changes (see Fig. 13). This is apparently due to enlargement of the complexes (O_2^{2-})(solid) and the formation of "molecules" of the type $(BaO_2)_2$ in solution:

$$\mathrm{O_2} + 2\mathrm{BaO} = (\mathrm{BaO_2})_2, \quad K_{64} = [(\mathrm{BaO_2})_2]/p_{\mathrm{O_2}}. \qquad (64)$$

The expression for K_{64} shows that in the case of reaction

(64), the concentration of excess oxygen will be proportional to p_{O_2}, in agreement with experiment[42]. It should be noted, however, that although the experimental data and thermodynamic calculations lead to the conclusion that the reaction of oxygen with MO involves mainly processes leading to the formation of electrically neutral defects in the form of the complexes (O_2^{2-})(solid) and $2(O_2^{2-})$(solid) or, which is the same thing, BaO_2 and $(BaO_2)_2$, this does not prove that reactions (57) and (58), leading to the formation of an "atomic" solution of oxygen in MO, or processes of ionised defect formation[65,66], do not take place. The experiment indicates merely that processes (62) and (64) predominate.

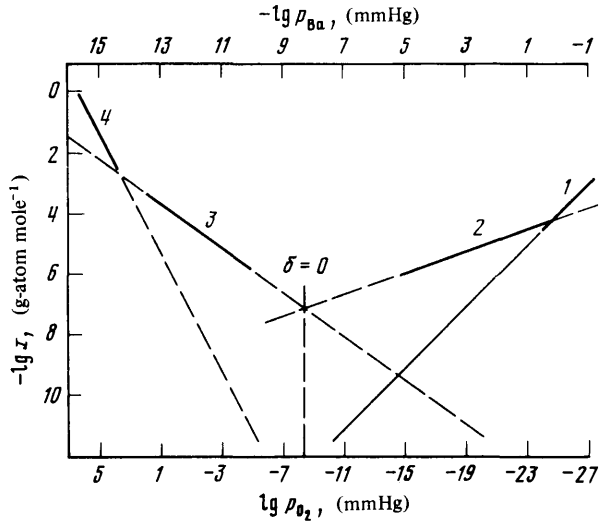


Figure 16. Solubility isotherms for excess Ba and oxygen in BaO at 1200°: *1*) $V_O^{\times}$, *2*) $V_O^{\cdot\cdot}$, *3*) complexes (O_2^{2-})(solid), *4*) complexes $(2O_2^{2-})$(solid).

Fig. 16 gives the solubility of defects of different kinds in BaO at 1200°. The equilibrium diagram for the defects in SrO, given in Fig. 10, is similar. This is quite regular, since BaO and SrO show closely analogous physicochemical properties. This is confirmed by direct measurement of the dependence of the concentration of the excess components on the vapour pressure of metal or oxygen and on temperature, and also by the study of the diffusion of Sr in SrO [67] and of Ba in BaO,[59] and by the absorption spectra of additively coloured crystals of SrO [28] and BaO.[29] These data, and the data for alkali metal halide crystals[60], indicate that the types of intrinsic point defect are similar in crystals of substances in the same homologous series.

The equilibrium diagrams for the defects in MO, given in Figs. 16 and 10, differ considerably from those proposed by Kroeger (see Figs. 14 and 15). Among others, two differences are particularly important: the first concerns the nature of the defects in an MO crystal having the stoichiometric composition, and the other is related to the fact that electrically neutral defects predominate in MO. These differences will be discussed in more detail.

2. Defects in Crystals of Compounds Having the Stoichiometric Composition

According to the hypothetical picture of the equilibrium for defects in BaO, proposed by Kroeger[60], the stoichiometry of BaO is due to the fact that the concentrations of V''_{Ba} and $V_O^{\cdot\cdot}$ or V'_{Ba} and $V_O^{\cdot}$, formed as a result of thermal disorder in the BaO crystal, are equal. The diagrams in Figs. 14 and 15 show that on coordinates $\lg x_i - \lg kp_M$ (where $kp_M = [V_O^{\times}]$), the solubility isotherms for V''_M and $V_O^{\cdot\cdot}$ (or V'_O and $V_O^{\cdot}$) exhibit mirror symmetry with respect to the straight line drawn perpendicular to the abscissa through the point of intersection of these isotherms (at which $\delta = 0$). The symmetry of the isotherms is characteristic of all the diagrams proposed by Kroeger[60] to illustrate the dependence of the concentrations of defects on the vapour pressure of the components in compounds of the type MO. This unavoidably leads to a situation in which, under conditions in which the crystal has the stoichiometric composition, the ratio of the concentrations of defects of "opposite" kinds, ensuring the symmetry indicated, should remain the same as that obtained in the examination of the so-called "internal thermal disorder" in the case where its production is not associated with interaction between the components of the crystal and the external medium[61]. In this approach (for example in the case of Frenkel disorder), the ratio of the concentrations of vacancies and interstitial atoms should be 1 : 1.

This idealised picture is far from reality. As correctly noted by Swalin[94], this relationship is not in fact necessary, and the concentration of vacancies may show absolutely no correlation with the concentration of interstitial atoms. The surface of the crystal may act as an independent source of vacancies, and the surrounding medium as a source of interstitial atoms. These considerations are also applicable to alkali metal halide crystals, which are usually regarded as model objects. In spite of the fact that in crystals having the stoichiometric composition, Schottky disorder, for example of the type[60]:

$$V_K^{\times} + V_{Cl}^{\times} \rightleftarrows O$$

is postulated, $V_{Cl}^{\times}$ and $(V_K^{\times})_2$ have been detected experimentally[60] under conditions of thermodynamic equilibrium between alkali metal halide crystals and their vapour, whereas $V_K^{\times}$ have not been found.

Similarly, it follows from the above experimental data that the stoichiometry of BaO is due to the fact that the concentrations of "unsymmetrical" defects, assumed to be $V_O^{\cdot\cdot}$ and (O_2^{2-}), [7,43,47,60] are equal. Studies of the mechanism of formation of defects in alkaline earth metal oxide crystals[11-14] have shown that their surface is the source of the defects existing in the bulk of the crystals.

Thus the existence of pairs of "symmetric" defects of the Schottky[69], Frenkel[68], or anti-structural[60] types, which are assumed to ensure the stoichiometry of the crystals, is not essential. Neither one-component nor multi-component crystals should be regarded as closed thermodynamic systems. As is usually done in the analysis of the phenomenon of departure from stoichiometry, for any crystals the formation of defects should be regarded as involving heterogeneous reactions including the exchange of material between the bulk of the crystal, its surface, and the coexisting phase (for example vapour). Under conditions of thermodynamic equilibrium,

both the composition of the bulk of the crystal and the composition of its surface layer are determined unambiguously by the temperature and composition of the equilibrium vapour phase.

3. Electrically Neutral Defects in MO

Studies of MO have shown that over a wide range of pressures and temperatures, the compositions of the compounds are determined chiefly by the concentration of electrically neutral defects, which are equivalent to atoms and molecules of the substances detected in the phases conjugate with MO. This last feature indicates that the chemical individuality of the components may be preserved on going from the conjugate phase to the dilute solution based on MO, and this makes it possible to reach certain conclusions regarding the nature of the electrically neutral defects in crystals of chemical compounds. The solid phase of a compound AB should apparently contain, albeit in extremely small quantities, all the components conjugate with it in the original system of phases[70]. When dissolved in AB, these components are electrically neutral defects, and under certain conditions, some of them may be present in appreciable concentrations (for example, Ba and BaO_2 in BaO). In the general case, the number of types of these electrically neutral defects (S) should be equal to the number of individual substances present in the phases conjugate with AB (and AB itself):

$$S = K + r,$$

where K is the number of independent components of the system, and r the number of independent chemical reactions.

Thus if the substances present in the phases in equilibrium with MO are known, it is possible to predict the types of possible electrically neutral defect in MO. Using data on the enthalpy and entropy of the reactions by which these substances are formed, it is possible in a number of cases to determine the conditions under which the appearance of significant quantities of the electrically neutral defects corresponding to these substances is possible. For example, the two possible mechanisms for the insertion of oxygen into MO: as MO_2 (see Eqn.(59)) and in atomic form (see Eqns. (57 and (58)), can be examined. As shown above (see Eqn. (61)):

$$\frac{\partial \ln x_{MO_2}}{\partial T} = (\Delta H_p + \Delta \bar{H}_{MO_2})/RT^2.$$

Similarly, for the solution of oxygen in atomic form,

$$\frac{\partial \ln x_O}{\partial T} = (\Delta H_{diss} + \Delta \bar{H}_O)/RT^2,$$

where ΔH_{diss} is the heat of dissociation of O_2 molecules to form atoms, and ΔH_O the differential molar heat of solution of atomic oxygen in MO.

As a rule, the heats of solution of the products of a chemical reaction in one another are small compared with the heat of the chemical reaction. Thus the temperature dependence of the solubility of the excess oxygen is determined by the sign of the enthalpy of the corresponding chemical reaction. When the excess oxygen dissolves in MO as MO_2, then $(\partial \ln x_{MO_2}/\partial T) < 0$, since $\Delta H_r \ll 0$. For the solution of atomic oxygen, it is to be expected that $(\partial \ln x_O/\partial T) > 0$, since $\Delta H_{diss} \gg 0$. Thus increase in temperature should lead to an increase in the concentration of atomic oxygen in the solid solution and a decrease in the concentration of MO_2. At high temperatures, the former may predominate; in this case the solubility isobar obtained on coordinates $\ln x_O - 1/T$ may pass through a minimum.

Analysis of the equilibrium constants of the reactions involved in the formation of the electrically neutral defects shows that the concentration of all types of electrically neutral defects formed by the introduction of excess oxygen increases with increase in p_{O_2}; similarly, the concentration of electrically neutral defects corresponding to excess Ba increases with increase in p_{Ba}. Close to the solidus line, the composition of the compound is determined chiefly by the concentration of electrically neutral defects. In fact, the separation of a new phase should probably be preceded by the formation of its nuclei within the original phase in the form of electrically neutral defects (one-particle or complex), corresponding to atoms and molecules of the substance being liberated.

V. PROPERTIES OF THE SURFACE AND THE NATURE OF THE EMITTING POWER OF MO CRYSTALS

Studies devoted to the investigation of the physicochemical character of the emitting power of an oxide cathode have a long history, but there is still lack of agreement on this question. One of the most fundamental problems still concerns the role of the bulk and surface properties of MO crystals in the phenomenon of the production of emitting power in the cathode. A widely encountered view, reflected in a number of monographs and reviews[71-73], is that an oxide cathode can be regarded as a semiconductor, the work function of which is determined by the concentration and energy state of the donor centres in the bulk of the crystal. A less widespread view is that the surface plays a decisive role in the phenomenon of electron emission from an oxide cathode[11,12,74-76]. The appearance of new data on the composition of the surface of MO crystals[36,37] and on the influence of the vapour of the alkaline earth metals on the emission and electrical conductivity of an oxide cathode[13,14,77-79] gives grounds for a more detailed examination of the relationship between the emission properties of a cathode and the properties of the surface of its oxide coating.

1. Non-stoichiometry of the Surface of MO Crystals

Experimental proof of the preferential localisation of excess M on the surface of MO crystals under the operating conditions of an oxide cathode were first obtained by the authors of the present review[31,32] and later by others[11,33]. A systematic study was made of the adsorption isotherms for Ba on the surface of BaO and for Sr on the surface of SrO [36,37] at 1000° and 1150° under conditions in which the pressure of oxygen over MO was greater by 4–6 orders of magnitude than the vapour pressure of M (calculated from Eqn. (50)) (the results are described above and given in Figs. 2 and 3). In spite of this, no significant adsorption of oxygen on the oxide surfaces was observed[36,37,47]. Thus in the analysis of the isotherms for the adsorption of M on MO it was possible to neglect the presence of oxygen.

Examination of various equations for the adsorption isotherms showed that the experimental data can be described by Temkin's equation for the adsorption isotherms for the case of a non-uniform surface[38]:

$$\Gamma_M = A \lg p_M + B, \quad (65)$$

where Γ_M is the quantity of adsorbed substance, g-atom cm^{-2}; and A and B are constants at a given temperature. The equations for the adsorption isotherms, given in Fig. 17 on coordinates $\Gamma_M - \lg p_M$, have the form

$$\Gamma_{Ba} = 7.7 \cdot 10^{-13} \lg p_{Ba} + 3.8 \cdot 10^{-12}; \text{ (at 1000° for Ba on BaO)}; \quad (66)$$

$$\Gamma_{Ba} = 9.4 \cdot 10^{-13} \lg p_{Ba} + 10.0 \cdot 10^{-12} \text{ (at 1150° for Ba on BaO)}; \quad (67)$$

$$\Gamma_{Sr} = 6.6 \cdot 10^{-9} \lg p_{Sr} + 8.7 \cdot 10^{-12} \text{ (at 1150° for Sr on SrO)}. \quad (68)$$

The isosteric heat of adsorption[38] of Ba on BaO, estimated approximately from two isotherms, is given by the equation:

$$q_{st} = 1.5 \cdot 10^2 (1 - 3 \cdot 10^{15} \Gamma_{Ba}) \text{ (kcal mole}^{-1}\text{)}. \quad (69)$$

Temkin's isotherm equation is applicable only if the experimental data on coordinates $\Gamma_M - \lg p_M$ are approximated by a straight line and if the slopes of the isotherms are proportional to the absolute temperature and the dependence on Γ_M is linear[38]. These requirements are met approximately by the isotherms for the adsorption of M on MO.

The adsorption of M on the surface of MO can be regarded as the solution of the excess metal in the surface layer of MO to a thickness of 1–3 molecular layers (this is the usual procedure in the analysis of the composition of the surface of solutions[80]). The concentration of M on the surface, calculated for one monolayer of MO ($x_M^{surface}$) is of the order of 10^{19} cm^{-3} (see Fig. 17). Under the same conditions, the concentration of excess M in the bulk of the crystals of BaO and SrO is only 10^{14}–10^{16} cm^{-3}.

For an understanding of the electronic processes taking place in MO specimens having a highly developed surface, it is important to compare the changes in the compositions of the surface and the bulk of MO crystals with change in the conditions of their equilibrium with the vapour of their own components. It may be assumed beforehand that the surface of the crystal contains both excess metal and oxygen in adsorbed form. This makes it possible to apply to the description of the composition of the surface the concept of departure from stoichiometry. The adsorption isotherms in Fig. 17 show that the concentrations of the excess adsorbed metal and oxygen may become of similar magnitude at values of the vapour pressure of M at which $\Gamma_M \simeq 0$. In a first approximation, it is assumed that at this point the concentrations of the quasi-excess components (M and O) on the surface are the same, that is that the surface has the stoichiometric composition. The surface is apparently enriched in excess metal at high values of p_M, and in oxygen at low values.

Comparison of Figs. 13 and 17 shows that at certain vapour pressures, not only the magnitude but also the sign of the departure from stoichiometry in the MO crystals may be different in the bulk and on the surface. The point corresponding to the stoichiometric ratio of the concentrations of quasi-excess M and O dissolved in the bulk of the crystal lies at much lower oxygen pressures than the analogous point for the quasi-excess components localised on the surface. From this it follows, in particular, that in a certain range of values of p_{O_2}, the conductivity of the crystal close to the surface may be different in character from that in the bulk: the surface is enriched in donors, whereas the bulk may be enriched in acceptors.

This phenomenon, described as inversion of the conductivity[81], has been observed experimentally for a number of semiconductors. Measurements of the electrical conductivity (σ) of polycrystalline specimens of alkaline earth metal oxides[82,83] and their solid solutions[84] showed that the isotherms giving the dependence of σ on p_{O_2} (Fig. 18) have a minimum, which corresponds to the point at which the conductivity of the oxide changes sign (if it is assumed that the mobilities of the holes and electrons are the same). Since the concentration of donor centres in the bulk of the MO crystals under the conditions of the measurements was extremely low, the high value of the

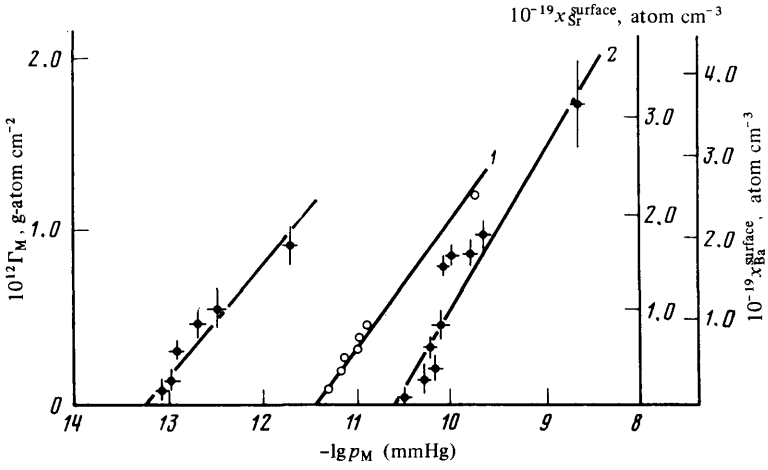


Figure 17. Isotherms for the adsorption of M on MO: *1*) Ba on BaO at 1000°;[36] *2*) Ba on BaO at 1150°;[36] *3*) Sr on SrO at 1150°.[37]

n-type conductivity could only be due to surface donor centres. Thus the minimum point on the graph giving the dependence of σ on p_{O_2} should have been situated in the range of oxygen pressures corresponding to a sharp decrease in the adsorption of M. Comparison of the experimental dependence of the electrical conductivity of BaO on p_{O_2} [82] (Fig. 18) with the p–T–x diagram of BaO for specimens having a highly developed surface (Fig. 8) supports this suggestion. The comparatively small difference (1.5–2 orders of magnitude) between the values of p_{O_2} corresponding to the stoichiometric point on the diagram in Fig. 8 and the electrical conductivity minimum in Fig. 18 may be associated with differences in the degree of ionisation of the donors and acceptors, and a difference in the mobilities of the electrons and holes.

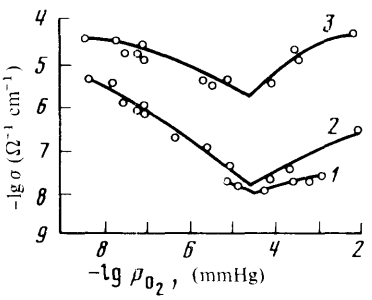


Figure 18. Dependence of the conductivity of BaO on p_{O_2}:[82] *1*) at 617°, *2*) at 637°, *3*) at 757°.

2. Nature of the High Emitting Power of MO Crystals

The adsorption of M on the surface of MO crystals is characterised by a high isosteric heat of adsorption, which is strongly dependent on the degree of covering of the surface. This is characteristic of the processes of chemisorption on semiconductors[81], when the points of adsorption on the surface of the adsorbent are energetically non-equivalent. The adsorption of M on MO may be expected to lead to the formation, on the surface, of several types of donor centre, for which the positions of the energy levels relative to the energy level of electrons in a vacuum will be different[75]. According to Vol'kenshtein[81], the high concentration of donors ($\sim 10^{12}$ cm^{-2}) on the surface of MO crystals makes it possible to regard it, from the viewpoint of its electronic properties, as "quasi-insulated" from the bulk. The existence of these surfaces was first predicted theoretically by Bardeen[85], and it has also been detected experimentally for a number of semiconductors; the work function of electrons from a semiconductor is independent of the position of the Fermi level in the bulk[81].

The conclusion that the surface of MO crystals plays a decisive role in the production of the emitting power of an oxide cathode, which follows from the results of adsorption measurements, is confirmed by studies[13,14,77–79,86–90] of the influence of the vapour of the alkaline earth metal or oxygen on the emission of a cathode and on the high-temperature electrical conductivity of the oxide coating of the cathode.

Nikonov and Beinar[13,14,78] made a detailed study of the emission of oxide cathodes in Ba vapour. The influence of a stream of Ba having an intensity of 1.2×10^{11}–1.6×10^{12} atom cm^{-2} s^{-1} on the emission current of oxide cathodes at 560–1350 K was studied[13]. At low temperatures, when the rate of deposition of Ba on the surface of the oxides of different alkaline earth metals was greater than the rate of its desorption, and the degree of covering of the surface by Ba atoms was much greater than that in the absence of the stream of Ba, a very marked increase in the emission current (I_e) was observed. At high temperatures, when the ratio of the forward and back streams of Ba changed, its influence on the emission decreased sharply, and finally disappeared at the highest temperatures. Measurements[14] at low Ba streams showed that I_e is directly proportional to the concentration of Ba atoms on the surface of the oxide coating (Fig. 19). Similar results were obtained when I_e for oxide cathodes was measured in a stream of Ba.[86–90]

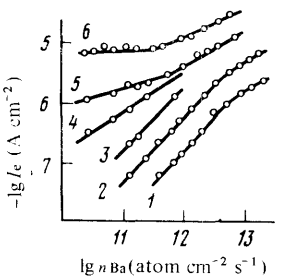


Figure 19. Dependence of the thermo-electronic emission current (I_e) of SrO on the magnitude of the stream of Ba vapour at different cathode temperatures: *1*) 317°, *2*) 347°, *3*) 422°, *4*) 482°, *5*) 537°, *6*) 607°.[13]

In contrast to the above measurements of emission, carried out under obviously non-equilibrium conditions, the influence of Ba on the properties of an oxide cathode has also been studied[77–79] under conditions close to equilibrium. Studies of the dependence of the emission current of an oxide cathode on p_{Ba} [79] showed that I_e changes very little with change in p_{Ba} (Fig. 20). Similar results were obtained in a study[77] of the electrical conductivity and thermo-e.m.f. of a BaO coating. The study[77] was based on the assumption[91,92] that at high temperatures (>800 K), the electrical conductivity of the porous coating of an oxide cathode is determined by free electrons emitted by the granules in the pores of the coating; a correlation should therefore exist between the electrical conductivity of the coating and the emitting power of the cathode. Measurements showed that at temperatures higher than 700°, the electrical conductivity (and also I_e [79]) increase very little with change in p_{Ba} from 8×10^{-7} mmHg to 2×10^{-5} mmHg. Under the same conditions, the thermo-e.m.f. of the oxide coating was only 150–200 μV K^{-1}. This value is typical of semiconductors in which the Fermi level lies at the bottom of the conductivity zone; this corresponds[77] to a high concentration of electrons in the crystal ($\sim10^{19}$ cm^{-3}). Since the concentration of donor centres in the bulk of BaO is lower by several orders of

magnitude, it was suggested[77] that there is an appreciable concentration of defects at the surface of the BaO crystals. In fact, the above concentration of electrons in BaO crystals coincides with that found experimentally from adsorption measurements of the concentration of excess Ba on the surface of BaO (see Fig. 17). The isothermal dependence of the concentration of Ba atoms on p_{Ba} is weak and logarithmic (see Eqns. (66)–(68)), and this explains the weak dependence of I_e and σ on p_{Ba} under conditions close to equilibrium.

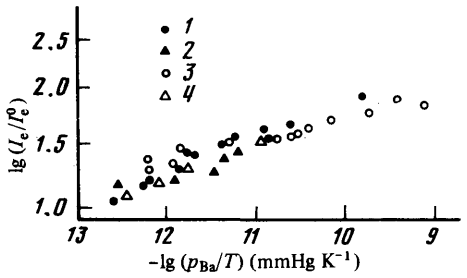


Figure 20. Dependence of the relative increase in the emission for (BaSr)O on p_{Ba} at 800° [79] from four series of experiments (*1–4*).

The change in the state of the surface of MO crystals may also provide a qualitative explanation for the phenomenon of "poisoning" of oxide cathodes by oxygen. The pressure of oxygen over BaO crystals at which a sharp decrease in the quantity of Ba atoms begins can be calculated. At 1150°, $\Gamma_{Ba} = 0$ at $p_{Ba} = 2\times10^{-9}$ mmHg, and at 1000°, $\Gamma_{Ba} = 0$ at $p_{Ba} = 2\times10^{-12}$ mmHg (see Fig. 17). The dissociation constant of BaO (Eqn. (27)) can be used to calculate the oxygen pressures corresponding to these values of p_{Ba}: at 1150°, $p_{O_2} = 7\times10^{-3}$ mmHg, and at 1000°, $p_{O_2} = 2\times10^{-5}$ mmHg. This explains the familiar experimental fact[72] that with increase in temperature, the "poisoning" of an oxide cathode takes place at higher oxygen pressures.

These experimental studies of the properties of the surface and their relationship to the emitting power of an oxide cathode apparently indicate that the state of the surface has a decisive influence on the emitting properties of alkaline earth metal oxides. In recent years, the theory of the oxide cathode having surface donor centres has been actively developed by Nikonov[75,76] and Zalm[93].

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Advances in the Study of the Stereochemistry of Quinolizidines, Indolizidines, and Pyrrolizidines

I.M.Skvortsov

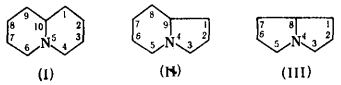
The results of studies on the stereochemistry of quinolizidines, indolizines, and pyrrolizidines are examined. Attention is concentrated on the application of non-spectroscopic methods in the determination of the configurations and preferred conformations. The possibilities and limitations of various physical and physicochemical methods in the study of the stereochemistry of the above 1-azabicyclic compounds are demonstrated.
The bibliography includes 193 references.

CONTENTS

I. Introduction 262
II. Configurational assignment of the bases 262
III. Conformational analysis of the bases 270
IV. The configurations and conformations of the bases and quaternary salts protonated at the nitrogen atom 274

I. INTRODUCTION

Quinolizidine (I), indolizidine (II), and pyrrolizidine (III) constitute the basis of many plant alkaloids and synthetic medicinal drugs. Interest in the stereochemistry of compounds (I)–(III) and their derivatives, whose specific features are due to the capacity of the bicyclic systems for reversible *cis*–*trans* transformations as a result of the inversion of the pyramidal nitrogen atom, is therefore quite justified.



(I) (II) (III)

Quinolizidines have now been investigated in greater detail as regards their stereochemistry, a comparatively few studies have been made on indolizidines, and the investigation of the conformational behaviour of compounds of the pyrrolizidine series is in essence only just beginning. We shall not consider the structures of quinolizidine, indolizidine, and pyrrolizidine alkaloids, with the exception of a few individual interesting examples, because since 1971 the appropriate compilations are being published annually[1-4]. A number of reviews have been devoted to the stereochemistry of pyrrolizidines.[5-8] In reviews[9,10] of stereochemical studies on compounds with a nodal nitrogen atom by spectroscopic methods quinolizidines,[9,10] indolizidines,[9] and (very briefly) pyrrolizidines [9] are considered among other heterocycles.

Analysis of research on the stereochemistry of compounds in Groups (I)–(III) shows that non-spectroscopic methods for the determination of steric structures have been used continuously. However, despite their evident importance, they have been frequently eclipsed by the effective achievements of infrared and NMR spectroscopy and have not been surveyed in the review literature.

Many similar stereochemical problems in the quinolizidine, indolizidine, and pyrrolizidine series have been solved by the same procedures, which shows that they have common features for the given series of compounds and makes it useful in the subsequent discussion to arrange the studies in groups based on the methods underlying the solution of particular problems.

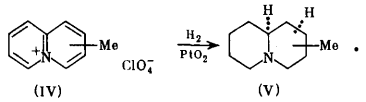
II. CONFIGURATIONAL ASSIGNMENT OF THE BASES

The problems of the configurational assignment and of the determination of the preferential conformations are sometimes closely related and are solved simultaneously. The systematic arrangement of data suggested in the present review is therefore sometimes somewhat conventional. The nomenclature adopted in the stereochemistry of 1-azabicyclic compounds is used in the description of the configurations[9].

1. The Employment of the Characteristic Features of the Stereochemistry of Catalytic Hydrogenation and of the Dependence of the Physical Properties of Isomers on Their Steric Structure

The configurational assignment of substituted quinolizidines, indolizidines, and pyrrolizidines, obtained by the catalytic hydrogenation of the corresponding quinolizidines, indolizines, and pyrrolizines, is based on the assumption of the preferential *cis*-addition of hydrogen by analogy with other aromatic systems[11].

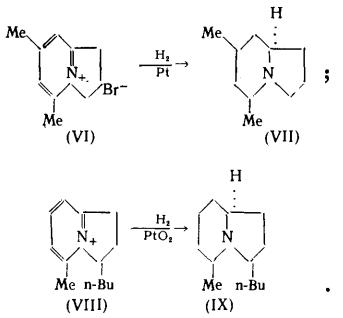
The hydrogenation of 1-, 2-, and 4-methyldehydroquinolizinium perchlorates (IV) [12] or 4-methyldehydroquinolizinium bromide[13] on PtO_2 resulted in the formation of isomers to which the *cis*-configuration (V) was attributed:



(IV) (V)

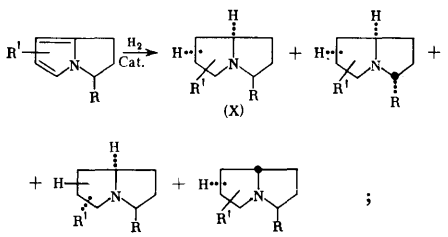
Dehydrogenation of the bromide (VI) in the indolizine series led to the isolation of *cis*-5,9-*H*-*cis*-7,9-*H*-5,7-dimethylindolizidine (VII) as the sole isomer[14] and the

reaction of the salt (VIII) gives *cis*-3,9-*H*-3-n-butyl-*cis*-5,9-*H*-5-methylindolizidine (IX) [15]:



The remaining three isomers of the last compound were obtained from the corresponding pyridine and pyrrole alcohols, the key process determining the configuration being the catalytic hydrogenation of these alcohols accompanied by the *cis*-addition of hydrogen [15].

As a result of hydrogenation, 5-methyl-,[16] 3,5-dimethyl-,[17] 5-hydroxymethyl-, 5-hydroxymethyl-3-methyl, [18,19] 5-(β-hydroxyethyl)-, 7-(β-hydroxyethyl)-,[20] and 7-ethoxycarbonyl-1,2-dihydropyrrolizine [21] and 7-ethoxycarbonyl-3*H*-pyrrolizine [22] give rise to mixtures of isomers in which compounds (X)†, with a relative *cis*-configuration at the carbon atom attached to the substituent R′, predominate [18]:

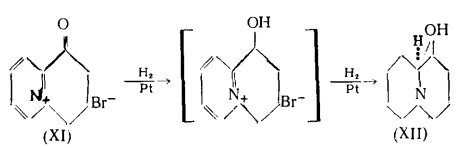


(R = H, Me; R′ = 5-Me, 5-CH_2OH, 5-$(CH_2)_2OH$, 7-$(CH_2)_2OH$, or 7-CO_2Et.

The hydrogenation of 1-methoxycarbonyl-7-oxo-6,7-dihydro-5*H*-pyrrolizine exhibits the same behaviour [23].

Examples of the stereoselective hydrogenation of aromatic systems with substituents in the "non-aromatic" half of the bicyclic system are formally similar but are nevertheless fundamentally different from the instances examined above. Here too isomers with the *cis*-configuration are formed preferentially, but the process selectivity is evidently ensured by the preferential adsorption of the compound hydrogenated from the sterically more accessible side [11].

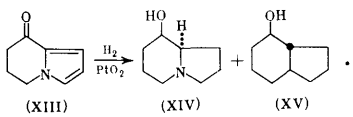
According to Swan's data [24], the hydrogenation of compound (XI) is completed by the formation of *cis*-1,10-H-1-hydroxyquinolizidine (XII):



Initially the carbonyl group is converted into a hydroxy-group, after which the ring is hydrogenated, hydrogen being attached to the angular $C_{(10)}$ atom from the side opposite to that of the hydroxy-group [24].

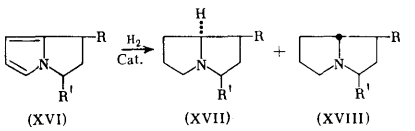
†Here and henceforth the symbol Cat. denotes a metallic catalyst.

The addition of hydrogen to 8-oxopyrrolo[1,2-*a*]piperidine (XIII) is less selective, the *trans*-isomer (XV) (24%) being formed together with the main product—the *cis*-isomer (XIV) (76%) [25]:



The *cis*-configuration at $C_{(3)}$ in the indolizine homologue (IX) is a consequence of the steric effect of the t-butyl group on the hydrogenation of compound (VIII). [15]

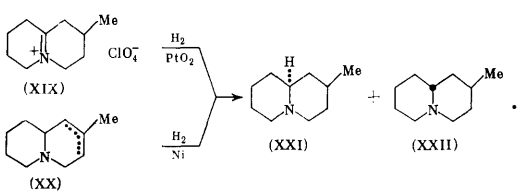
An analogous stereochemical effect is observed in the hydrogenation of 1,2-dihydropyrrolizidines and pyrrolizidines. 1,2-Dihydropyrrolizines (XVI) with alkyl groups in the 1- or 3-position are converted into mixtures of isomers (XVII) and (XVIII), among which compounds with the *cis*-configuration at $C_{(1)}$ or $C_{(3)}$ (XVII) predominate quantitatively [16,26-28]:



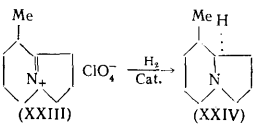
R = H, Me; R′ = H, Me, or t-Bu .

The hydrogenation of 1-methyl-3*H*-pyrrolizine in the presence of rhodium under mild conditions gives rise to *cis*-1,8-*H*-1-methylpyrrolizidine (*d,l*-heliotridane). [29] The stereochemistry of the hydrogenation of 1,2-dihydropyrrolizines with functional groups in the "non-aromatic half" of the bicyclic system [23,30,31] is also kinetically and not thermodynamically controlled, as was suggested by Adams et al. [32] The reaction leads to the formation of thermodynamically less stable isomers with the *cis*-configuration of the substituted atoms of the bicyclic system—the steric effects of the substituent has a decisive influence on the stereochemical result of the hydrogenation.

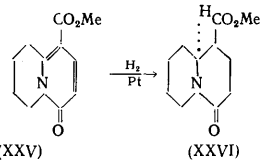
The preferential *cis*-addition of hydrogen in the hydrogenation of compounds with multiple bonds [11] and the adsorption of the substrate on the catalyst from the most accessible side were taken into account in the configurational assignment of quinolizidines, indolizidines, and pyrrolizidines obtained from the corresponding partly unsaturated derivatives. The catalytic addition of hydrogen to compounds (XIX) or (XX) yields mixtures of epimeric 2-methylquinolizidines (XXI) and (XXII). The *cis*-configuration was attributed to isomer (XXI), which is the dominant product in both cases [33]:



The hydrogenation of the perchlorate (XXIII) to *cis*-8,9-*H*-8-methylindolizidine (XXIV) takes place more selectively [34]:

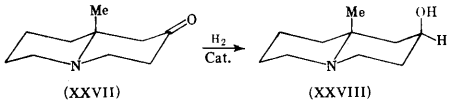


On platinum, hydrogen undergoes *cis*-addition to the $C_{(1)}$–$C_{(10)}$ bond in compound (**XXV**) and the quinolizidine derivative (**XXVI**) with the relative *cis*-configuration at $C_{(1)}$ is obtained[35]:



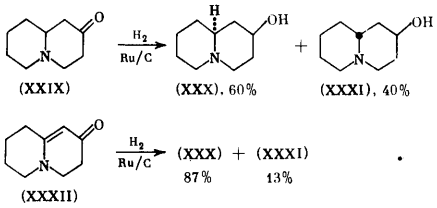
(XXV) (XXVI)

It has been shown that 10-methyl-2-oxoquinolizidine (**XXVII**) has a *trans*-junction between the two rings[36]. Bohlmann et al.[36] believe that the catalytic hydrogenation of the carbonyl group therefore leads to compound (**XXVIII**) with an axial hydroxyl owing to steric hindrance to adsorption generated by the methyl group:



(XXVII) (XXVIII)

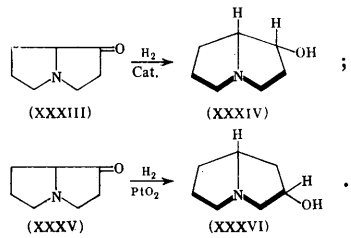
A conclusion has been reached[37,38] about the configurations of the epimeric 2-hydroxyquinolizidines by comparing the ratios of the isomers obtained on catalytic hydrogenation of 2-oxoquinolizidine (**XXIX**) and $\Delta^{1,10}$-2-oxoquinolizidine (**XXXII**) under identical conditions:



The authors attribute the *cis*-configuration (**XXX**) to the epimer whose fraction increases on transition from (**XXIX**) to (**XXXII**), assuming that the bulk of the hydrogen atoms add to molecules of compound (**XXXII**) from the same side in the course of a single adsorption step.

In the general case the hydrogenation of 1-oxoquinolizidine,[24,37] 2-and 3-oxoquinolizidines, and $\Delta^{1,10}$-2-oxoquinolizidine [37] under different conditions is not distinguished by high stereoselectivity and cannot serve as a basis for the configurational assignment of the 1-, 2-, and 3-hydroxyquinolizidines formed.

On the other hand, the catalytic addition of hydrogen to carbonyl-containing pyrrolizidines (**XXXIII**) and (**XXXV**) is characterised by its stereospecificity and, together with data derived from other methods, can serve as evidence in support of the configurations of the aminoalcohols (**XXXIV**) and (**XXXVI**) illustrated below[30]:



(XXXIII) (XXXIV)

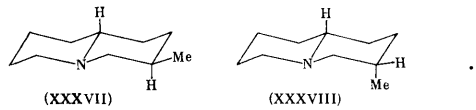
(XXXV) (XXXVI)

The different types of behaviour of carbonyl derivatives of quinolizidine and pyrrolizidine during catalytic reduction are probably due to geometrical factors.

In many other examples dehydropyrrolizidines containing a multiple bond in the ring combine catalytically with hydrogen from the sterically least hindered side of the molecule regardless of the position of the multiple bond, which leads to the *cis*-configuration of the new asymmetric centre in relation to $C_{(8)}$.[39-43] In the solution of the problems of the configurational assignment of isomers of more complex systems—deoxynupharidine,[44] perhydrobenzo[*c*]quinolizine,[45] 9-azasteroid cyclic systems[46], and 6-disubstituted perhydrobenzo[*c*]quinolizines,[47] whose synthesis involves a hydrogenation range—the concept of the catalytic *cis*-addition of hydrogen was taken into account.

Thus the characteristics of the stereochemistry of the catalytic hydrogenation can be used widely in the determination of the configurations of isomers. Caution must be exercised in reaching conclusions primarily in those cases where the hydrogenation is carried out under conditions permitting isomerisation, which is observed at high temperatures and when catalysts (for example, palladium) promoting the isomerisation process are used.

The examples described by Moynehan et al.[12] must be regarded as exceptions. The hydrogenation of 3-methyldehydroquinolinium perchlorate is distinguished by low stereoselectivity. Assuming the conformation with a *trans*-junction for quinolizidine and its methyl derivatives, Moynehan[12] attributed on the basis of the conformational rule[48] the structure (**XXXVII**) (*trans*-configuration) to the 3-methylquinolizidine with the lower refractive index and the *cis*-configuration (**XXXVIII**) to the more strained epimer with the higher refractive index:



(XXXVII) (XXXVIII)

The remaining three pairs of epimeric methylquinolizidines obey the conformational rule[12].

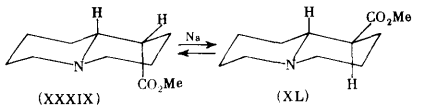
Among the epimeric pairs of 3-hydroxyquinolizidines,[38] 1-,[30] 2-,[30] and 8-hydroxyindolizidines,[25] and 3-hydroxymethylpyrrolizidines,[19] the isomers with an intramolecular hydrogen bond have lower boiling points.

2. Thermodynamic and Kinetic Methods

An *a priori* estimate of the relative thermodynamic stabilities of the isomers of substituted quinolizidines, indolizidines, and pyrrolizidines has served in a number of instances as the starting point for their configurational assignment. If the formation of both epimers is possible in thermodynamically controlled reactions, then the isomer with a larger store of free energy predominates quantitatively.

Assuming a *trans*-junction between the rings for simple monosubstituted quinolizidines, one may reach the conclusion, analogous to that of Leonard and Ryder[49], that the thermodynamically preferred isomer has the substituent in the equatorial position. Evidently among indolizidines this isomer has the equatorial substituent in the six-membered ring or the substituent is in a pseudoequatorial position in the five-membered ring. In the pyrrolizidine series, among the epimers differing in the position of the substituent at any one carbon atom, the isomers with the *trans*-configuration are thermodynamically more stable (see, for example, Refs. 30, 39, and 50) being more favoured by the non-bonding interactions. This rule is apparently valid for all monosubstituted pyrrolizidines.

The epimerisation of 1-substituted quinolizidines—lupinine [49,51-53] and the methyl ester of lupininic acid (XXXIX) [49,54]—under the influence of sodium or sodium methoxide has been described. According to Cookson's data[54], equilibrium is reached when 15% of the *cis*-isomer (XXXIX) and 85% of the *trans*-isomer (XL) is attained:

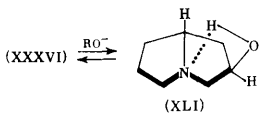


(XXXIX) (XL)

Other examples of the application of the isomerisation reaction in the configurational assignment of quinolizidines have been described[55-58].

In the pyrrolizidine series epimerisation was completed in most of the known instances by the formation of virtually only one compound and one can therefore attribute to the latter the *trans*-configuration quite reliably. The isomerisation of substituted pyrrolizidines under the influence of acids[50], bases[22,30,42,59], and metallic catalysts[17-20,28] has been investigated. The epimerisation can occur at the first[21,30,42,50,59], third[18-20,28], and third and fifth[18,19] carbon atoms with different substituents—alkyl[17,28] and hydroxyalkyl[18-20] groups as well as hydroxy-,[30] carboxy-,[50] and alkoxycarbonyl [22,42,59] groups.

Incomplete epimerisation of compound (XXXVI) led to a mixture of epimers (XXXVI) and (XLI) in proportions of 2 : 3:

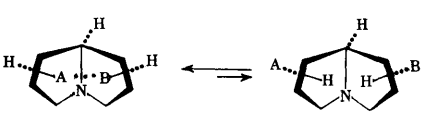


(XLI)

In this particular case the isomer (XLI) is thermodynamically preferred owing to the liberation of energy as a result of the formation of an intramolecular hydrogen bond on transition from (XXXVI) to (XLI) and is not caused by the difference between the non-bonding reactions in epimers (XXXVI) and (XLI).[30]

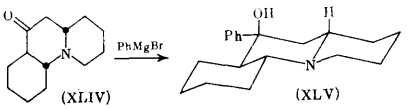
It has been shown[50] that only the asymmetric centre at $C_{(1)}$ is involved in the isomerisation of optically active pyrrolizidine-1-carboxylic acids and there is no racemisation.

The method described here can be extended to the pyrrolizidine systems in which the difference between the free energies of the epimers is determined mainly by the difference between their non-bonding interactions. The possibility of the existence of di- or poly-substituted pyrrolizidines, in which the attraction energy of the substituents, for example A and B, in isomer (XLII) is greater than their repulsion energy, can be postulated. Under equilibrium conditions, isomer (XLII) then predominates and not isomer (XLIII), as might have been expected on the basis of the formal analogy with the literature data.



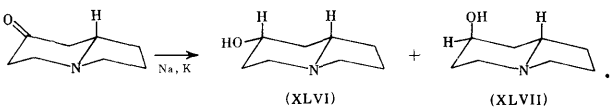
(XLII) (XLIII)

The hydride reduction of 1- and 2-oxoquinolizidines yields alcohols with an equatorial hydroxy-group (*trans*-junction between the rings) as the thermodynamically more stable isomers[24,36]. Similarly the configuration (XLV) with the phenyl group in an equatorial position has been attributed to the single isomer formed in the reaction of compound (XLIV) with phenylmagnesium bromide[47]:



(XLIV) (XLV)

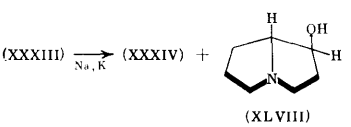
The configurations of 7-hydroxyindolizidines (XLVI) and (XLVII) have been determined from the reduction of 7-oxoindolizidine with sodium or potassium in alcohol:



(XLVI) (XLVII)

Isomer (XLVI) predominates quantitatively (96–98%) in a mixture with (XLVII) owing to its greater thermodynamic stability[25].

Similarly, on reduction with sodium or potassium, 1-oxopyrrolizidine (XXXIII) is converted into a mixture of epimers (XXXIV) (10–20%) and (XLVIII) (80–90%).[30] However, under the conditions of the reduction of compound (XXXIII) with sodium tetrahydroborate in water or with lithium tetrahydroaluminate, isomer (XXXIV) is formed as the main product (60%) [30]:



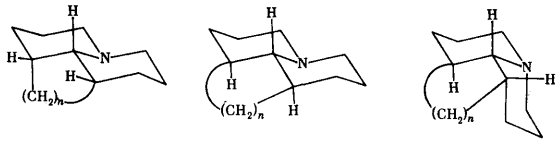
(XLVIII)

The greater reactivity of the substituent occupying the equatorial position compared with the axial position in the quinolizidine and indolizidine series or the greater reactivity of the substituent in the *exo*-position compared with the *endo*-position in pyrrolizidines may lead to the occurrence of side reactions, which alter the initial ratio of the isomers. The relevant findings have been obtained for substituted quinolizidines[60].

Kinetic methods are widely used in studies undertaken to determine the configurations of the 1-azabicyclic substances under discussion. The esters derived from the isomeric 2-hydroxyquinolizidines (XXX) and (XXXI) showed distinct differences in hydrolysis. The isomers with the sterically exposed equatorial functional group are hydrolysed faster than those with the more shielded axially oriented ester fragment[36]. In the acylation of isomeric 1-hydroxy-3-oxoindolizidines by benzoyl chloride the ester gives rise to only one of them[61]. This difference between the reactivities is explained by the fact that the hydroxy-group in the acylated isomer occupies a more accessible equatorial position and it occupies the axial position in the inactive isomer[61]. Comparison of the rate constants for the oxidative dehydrogenation of the three isomeric hexahydrojujolidines permitted a configurational assignment of the isomers[62].

In the solution of stereochemical problems comparison of the rate constants for the quaternisation of the isomers or a qualitative comparison of their reactivities in this reaction proved to be fruitful. The configurational assignment of cyclopenta[*ij*]quinolizidines (XLIX)–(LI) [63] was carried out; among these isomers, compounds (XLIX) and (L) behave in the reaction with methyl iodide similarly to compounds (LII) and (LIII). The configurations of the latter and of (LIV) were found by other methods[62] and are consistent with the rate constants for the reactions with

methyl iodide[64].

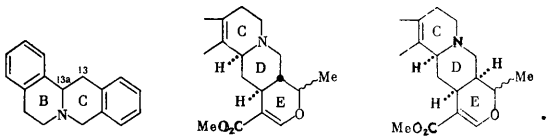


(XLIX), $n = 2$; (L), $n = 2$; (LI), $n = 2$;
(LII), $n = 3$ (LIII), $n = 3$ (LIV), $n = 3$

The molecules of the isomer (LI)‡ are chiral; the isomer was partly resolved into optical enantiomers and this fact served as an argument in support of the configuration shown[63].

Qualitative comparison of the rates of reaction of isomeric perhydrobenzo[*c*]quinolizines with methyl iodide led to stereochemical assignments in agreement with data obtained by other methods[45].

The rate of quaternisation of tetrahydroprotoberberines—derivatives of dibenzoquinolizidine (LV)—depends on the type of junction between the B and C rings, which is determined by the configuration at $C_{(13)}$.[65]



(LV) (LVI) (LVII)

Information about the junction between the D and E rings in heteroyohimbine alkaloids was obtained from kinetic measurements. Compounds of type (LVI) were methylated at a higher rate than those of type (LVII). The configuration with the *trans*-junction of the D and E rings, in which the nitrogen atom is more accessible than in compounds of group (LVII) having the *cis*-junction between the D and E rings, was attributed to the former compounds[66,67]. Similarly yohimbine reacts with methyl iodide 40 times faster than α-yohimbine.[65]

The configurations of 9-methoxy-3,12*b*-dimethyl-1,2,3,4,6,7,12,12*b*-octahydroindolo[2,3-*a*]quinolizidines[68] and biphenyl alkaloids with quinolizidine fragments—lythrine, vertine,[69] vertaline, and decaline[70]—were determined with the aid of data for the kinetics of reactions of these bases with methyl iodide.

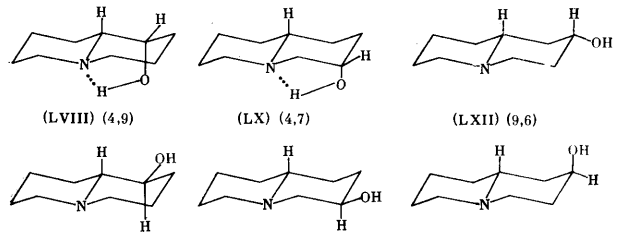
Various criteria for the determination of the stereochemistry of steroid indolizidines were examined by Kolb and Stefanovič[71], who found that the kinetic data for the quaternisation of isomeric compounds by methyl iodide constitute a more reliable basis for stereochemical assignments in the given group of compounds than spectroscopic methods. Qualitative observation of the course of competitive quaternisation of isomeric 3-substituted pyrrolizidines, first proposed for the determination of the configurations of epimeric 3-methyl pyrrolizidines,[72] can apparently be regarded as a general method for the determination of the steric structure of 3-substituted pyrrolizidines. It is based on the fact that isomers with the *trans*-configuration have a more shielded lone electron pair at the nitrogen atom and hence the rate of their reaction with alkyl halides is lower than that of the isomers having the *cis*-configuration. For correct conclusions, it is necessary that the quaternisation reaction should involve a decrease of the content of one of the epimers when its fraction in the mixture of isomers is 50% or less. The steric structure of isomeric 3,5-dimethylpyrrolizidines,[17] 3-hydroxymethylpyrrolizidines,[18,19] and 3-(β-hydroxyethyl)pyrrolizidines[20] were established with the aid of this method.

3. Chromatographic Methods

Bohlmann and coworkers[44,73] showed that the adsorbability of many compounds on alumina depends on the degree of shielding of the lone electron pair of the nitrogen atom. Comparison of the values of R_f or of the sequences in the elution of the isomers from the column[44,45,47,62,65,73-75] and examination of their models can therefore be a useful auxiliary method for the determination of the configuration. This same type of dependence has been found for perhydrobenzo[*c*]quinolizidines,[45] epimeric 6-methyl- and 6-ethylindolizidine-2-ones,[76] 3-methylpyrrolizidines,[72] and a number of saturated and unsaturated pyrrolizidine alcohols[77].

The application of gas–liquid chromatography (GLC) is particularly fruitful in the series of quinolizidines, indolizidine, and pyrrolizidine alcohols. The configurational assignments were most convincing for isomers one of which was capable of forming a relatively stable intramolecular hydrogen bond, while the other lacked this capacity by virtue of geometrical conditions.

In contrast to 2-hydroxyquinolizidines [compounds (LXII) and (LXIII)], the epimeric 1-hydroxyquinolizidines [compounds (LVIII) and (LIX)] and 3-hydroxyquinolizidines [compounds (LX) and (LXI)] have significantly different retention parameters§ on the polar phase Carbowax-20M.[38] Evidently epimers with stronger intramolecular hydrogen bonds should have shorter retention times than epimers with weaker hydrogen bonds or epimers which do not form such bonds at all. If the form with the *trans*-junction is adopted as the preferred conformation of the compounds considered on the basis of the adsorption observed in the range 2700–2800 cm^{-1}, then an intramolecular hydrogen bond can be formed only by compounds (LVIII) and (LX). The retention data for the isomers (LVIII)–(LXI) also indicate their configurational assignments, which have been confirmed by infrared spectroscopy[38].



(LVIII) (4,9) (LX) (4,7) (LXII) (9,6)

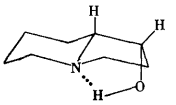
(LIX) (8,5) (LXI) (10,2) (LXIII) (8,6)

A distinct difference between the retention times has been observed for *cis*-3,10-*H*-3-hydroxymethylquinolizidine (LXIV) and *trans*-3,10-*H*-3-hydroxymethylquinolizidine (LXV)[60] and also for the stereoisomeric pairs of 3-hydroxymethyl-3-methylquinolizidines.[75] The configurational assignment of the epimeric 3-(4-chlorobenzyl)-quinolizidines has been made by analogy with compounds (LXIV) and (LXV), but the factors determining the retention of the isomers have not been discussed[60].

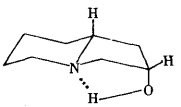
‡For simplicity, the formula of only one enantiomer is shown.

§Here and henceforth in this section the retention times in minutes are given in brackets.

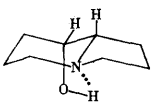
Similarly, comparison of the retention times in the GLC of 1-hydroxyindolizidines [compounds (LXVI) and (LXVII)], 2-hydroxyindolizidines [compounds (LXVIII) and (LXIX)], [30] and 8-hydroxyindolizidines [compounds (LXX) and (LXXI)] [25] permits conclusions about their configurations.



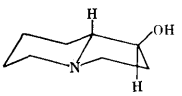
(LXVI) (3,7)



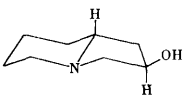
(LXVIII) (4,4)



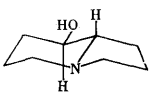
(LXX) (3,0)



(LXVII) (5,4)



(LXIX) (5,8)

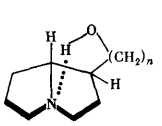


(LXXI) (5,7)

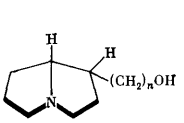
The epimeric 7-hydroxyindolizidines (LXVI) and (LXVII) do not form intramolecular hydrogen bonds and their retention times (6.4 and 7.1 min) [25] differ much less than for the preceding pairs of epimers.

Chalmers et al. [77] investigated the behaviour of pyrrolizidine alkaloids and certain saturated and unsaturated pyrrolizidine alcohols in GLC, thin-layer, and paper chromatography. Empirical correlations were found between the retention time on the siloxane polymer *SE*-30 and the orientation of the hydroxy-group in the 7-position: with the exception of retronecine and heliotridine, bases with a 7-*endo*-OH group (7β-OH). [77] The extremely weak intramolecular hydrogen bond in the isomer with a 7-OH *exo*-group evidently does not play a significant role in the retention of the compound on the stationary phase. The greater steric accessibility of the *exo*-hydroxyl is probably responsible for the greater energy of the interaction with the stationary phase than for the 7-*endo*-OH group. The same effect has been observed in the epimers (XLVIII) and (XXXIV) with the analogous difference between the positions of the hydroxy-group [30]. Even if a very weak intramolecular hydrogen bond is formed in compound (XLVIII), [30] it constitutes an unimportant factor in the interaction of the sorbate and the sorbent. Although weak, the intramolecular hydrogen bond, which is clearly present in the aminoalcohol (LIX), apparently weakens somewhat, compared with the epimer (XXXVI), the interaction with Carbowax-20M, which facilitates the separation of the isomers (XXXVI) and (XLI) by GLC. [30]

In GLC on both Apiezon L and on the polar stationary phase Reoplex-400, (±)-trachelanthamidine (LXXII), which has an intramolecular hydrogen bond, emerges from the column before its epimer (±)-isoretronecanol (LXXIII) [78] in which an intramolecular hydrogen bond cannot be formed for steric reasons.

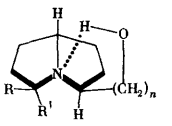


(LXXII), $n = 1$;
(LXXIV), $n = 2$(32)

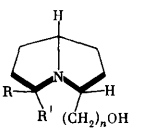


(LXXIII), $n = 1$;
(LXXV), $n = 2$(42)

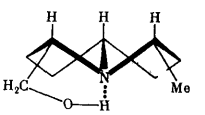
The stereochemistry of the diastereoisomeric 1-(β-hydroxyethyl)pyrrolizidines [compounds (LXXIV) and (LXXV)] [18,20], 3-hydroxymethylpyrrolizidines [compounds (LXXVI) and LXXVII)], [18,19] 3-(β-hydroxyethyl)pyrrolizidines [compounds (LXXVIII) and (LXXIX)], [18,20] 5-hydroxymethyl-2-methylpyrrolizidines, [19] and 5-hydroxymethyl-3-methylpyrrolizidines [compounds (LXXX)–(LXXXIII)]¶ [18,19] determines their different capacities for the formation of intramolecular hydrogen bonds and hence the energy of the interaction with the polar stationary phase.



(LXXVI), $n = 1$, R = R' = H (14);
(LXXVIII), $n = 2$, R = R' = H (16);
(LXXX), $n = 1$, R = Me, R' = H (32);
(LXXXII), $n = 1$, R = H, R' = Me (45).



(LXXVII), $n = 1$, R = R' = H (22);
(LXXIX), $n = 2$, R = R' = H (24);
(LXXXI), $n = 1$, R = Me, R' = H (70)

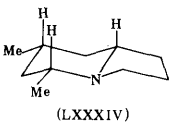


(LXXXIII)

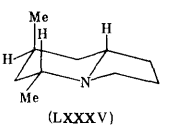
Analysis of the geometries of the isomers and data for the retention on Carbowax-20M were used in the configurational assignment of compounds (LXXIV)–(LXXXIII). [18,20]

The steric structures of the four isomeric 1,7-dimethylquinolizidines were determined [44] on the basis of chromatographic retention times of quinolizidine and 1-methyl-, 3-methyl-, and 1,7-dimethyl-quinolizidines. The shielding of the lone electron pair of the nitrogen in the isomeric perhydrobenzo[*c*]quinolizidines is regarded as a factor determining the difference between their retention times in GLC. [45] In the four isomeric 1-hydroxy-7-methylquinolizidines the orientations of the hydroxy- and methyl-groups are determined from the relative retentions obtained when the compounds are passed over a polar stationary phase [80], the positions of the methyl groups being established from the results of the GLC of methylquinolizidines [81]. An analogous method was used in the more complex case of the isomeric 1-hydroxy-1,7-dimethylquinolizidines. [82]

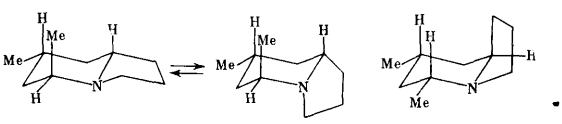
On the basis of the foregoing considerations, the relative retention times of cyclopenta[*ij*]quinolizidines (LXIX)–(LI), quoted by Schofield and Wells [63] without comment, may be regarded as independent confirmation of their structure, established by other methods. Quoting the results of the GLC of 5,7-dimethylindolizidines on the *SE*-52 stationary phase, Lüning and Lundin [14] do not relate the elution sequence of the isomers (LXXXIV), (LXXXV), (LXXXVI), and (LXXXVII) to their steric structure.



(LXXXIV)



(LXXXV)



(LXXXVIa) (LXXXVIб) (LXXXVII)

However, if account is taken of the set of data concerning the relation between the retention times and the structure of 1-azabicyclic compounds examined above, one may note that the interaction with the stationary phase is as a rule stronger for the less shielded lone electron pair of the

¶ Isomer (LXXXIII) is represented in the formulae as having a conformation with the *trans*-junction, which may be regarded as preferred according to the data of Skvortsov et al. [18] and by analogy with *cis*-3,8-H-*cis*-5,8-*H*-3,5-dimethylpyrrolizidine. [17,19]

nitrogen. The sequence in which the isomers are eluted from the column (stationary phase Carbowax-20M) is as follows: (LXXXIV)–(LXXXVII), 6-methyl-2-oxoindolizidine, and 6-ethyl-2-oxoindolizidine.[76]

Despite the evidently fruitful nature of the configurational assignment based on chromatographic data, one should note that in specific instances when there are difficulties in choosing the preferred conformation of the sorbate molecules at the instant of interaction with the sorbent, the stereochemical assignment becomes doubtful. A general deficiency of chromatographic methods for the solution of stereochemical problems involves the necessity to have at one's disposal at least two isomers at the same time in order to compare their chromatographic properties.

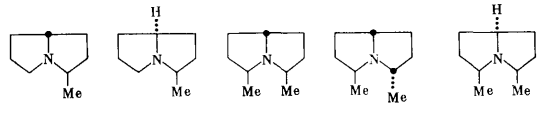
4. Basicities

The measurement of the pK_a values for the epimers of a series of quinolizidine and indolizidine alcohols in many cases permits conclusions about their configuration. Distinct differences between the pK_a values are shown by the epimeric pairs of 1-hydroxyquinolizidines [compounds (LVIII) and (LIX)] ($\Delta pK_a = 1.47$), 3-hydroxyquinolizidines [compounds (LX) and (LXI)], ($\Delta pK_a = 1.27$),[38] 1-hydroxyindolizidines [compounds (LXVI) and LXVII)] ($\Delta pK_a = 1.11$), 2-hydroxyindolizidines [compounds (LXVII) and (LXIX)] ($\Delta pK_a = 0.33$),[30] 8-hydroxyindolizidines [compounds (LXX) and (LXXI)] ($\Delta pK_a = 1.47$),[25] 1-hydroxy-1-methylquinolizidines ($\Delta pK_a = 1.1$), and 1-hydroxy-1-phenylquinolizidine ($\Delta pK_a = 0.9$).[83] Assuming the *trans*-junction of the rings in the above compounds, it can be clearly seen that the intramolecular hydrogen bond can be formed by isomers with axial or pseudoaxial hydroxy-groups, so that within each pair the epimer with the higher pK_a has the *cis*-configuration.

On average, smaller differences between the basicities are observed for the isomeric 2-hydroxyquinolizidines [compounds (XXX) and (XXXI)] ($\Delta pK_a = 0.33$),[38] 2-hydroxy-2-phenylquinolizidines ($\Delta pK_a = 0.20$),[84] 7-hydroxyindolizidines [compounds (XLVI) and (XLVII)] ($\Delta pK_a = 0.57$),[25] and 7-hydroxy-7-phenylindolizidines ($\Delta pK_a = 0.09$),[84] none of which forms an intramolecular hydrogen bond for steric reasons. In this case compounds with an axial hydroxy-group are stronger bases than the epimers with an equatorial hydroxy-group. In the series of heteroyohimbine alkaloids the pK_a reflects the degree of shielding of the nitrogen and is determined by the configuration of the compound[66,67].

The epimeric 1-hydroxypyrrolizidines (XXXIV) and (XLVIII) have similar pK_a values (10.35 and 10.25 respectively)[30]. A more distinct difference between the basicities is observed for 2-hydroxypyrrolizidines [compounds (XXXVI) and (XLI)] (pK_a = 10.25 and 10.42). The weak intramolecular hydrogen bond in the isomer (XLI) [30] is probably responsible for its high basicity[85].

Pyrrolizidine (III) and its homologues (LXXXVIII)–(XCII) have respectively pK_a = 11.68, 11.62, 11.94,[86] 11.46, 11.74, and 10.28.[87]



(LXXXVIII) (LXXXIX) (XC) (XCI) (XCII)

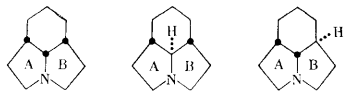
The lone pair of electrons on the nitrogen atom in compound (LXXXVIII) is more shielded by the methyl group than in its epimer (LXXXIX), which gives rise to steric hindrance to hydration and explains the weaker basicity of the former compound. The causes of the different basicities of the epimers (XC) and (XCI) are similar. The relatively low pK_a value of the isomer (XCII) is regarded as a direct consequence of its preferential state, in which there is a *trans*-junction[87].

5. Infrared Spectroscopy

The results of the application of infrared spectroscopy to the configurational assignment of numerous alcohols of the quinolizidine and indolizidine series as well as 1- and 2-hydroxypyrrolizidines have been summarised in a review[9].

The configuration of 2-hydroxyquinolizidines (XXX) and (XXXI), established by Bohlmann et al.[36], has been confirmed by a study of the frequencies and shapes of the absorption bands in the spectra of these epimers[38]. Dilute solutions of platynecine and retronecine [88] have 3467 and 3515 cm^{-1} absorption bands, which are characteristic of intramolecular hydrogen bonds, confirming the structure of these aminoalcohols[88]. The strong absorption by the hydroxy-groups involved in the intramolecular hydrogen bond is consistent with the structure of compounds (LXXVI) and (LXXX). The intramolecular hydrogen bond energies are approximately the same in the two compounds [$\Delta\nu$(OH) = 177 and 178 cm^{-1}].[19] A stronger intramolecular hydrogen bond [$\Delta\nu$(OH) = 380 cm^{-1}] is formed in the pyrrolizidine alcohol (LXXVIII) as a result of the more favourable geometry of the hydrogen bridge[20].

One of the three possible diastereoisomers of 1-azatricyclo[6,2,1,$0^{4,11}$]undecane, which absorbs in the range 2700–2800 cm^{-1}, has been isolated[89]. In choosing from the three possible configurations (XCIII)–(XCV), the last one was rejected, because, according to the authors[89], Bohlmann absorption can be manifested only by compounds with the configurations (XCIII) and (XCIV) (evidently with the *trans*-junction of the A and B rings). The structure (XCIII) was adopted tentatively[89].



(XCIII) (XCIV) (XCV)

The construction of models of isomers (XCIII) and (XCV) shows that in both cases the *cis*-junction of the A and B rings is free from strain and is therefore preferred to the *trans*-junction. The skeleton of the tricyclic compound (XCIV) is highly strained for both types of junction between the five-membered rings. We suggest that structure (XCIV) is therefore apparently more probable rather than structure (XCIII), since there should be no Bohlmann bands for the preferential *cis*-junction between the A and B rings in (XCIII). On the other hand, the existence of comparable amounts of conformations of isomer (XCIV) with the *cis*- and *trans*-junctions, the latter of which should be active in the range 2700–2800 cm^{-1}, may be expected.

6. NMR Spectroscopy

The successful application of ^1H NMR spectroscopy in the solution of stereochemical problems involving the series of quinolizidine and indolizidine derivatives is successfully dealt with in a review[9] and is based on the

analysis of the chemical shifts of the ring and methyl protons as well as the spin–spin coupling constants and the nature of the splitting of the signals. In studies which have not been included in the above review[9] it is possible to encounter new examples of the analogous use of the given method for the determination of the configurations of quinolizidine[75,90-92], indolizidine,[76,93] and pyrrolizidine[17,28,42,59,94-99] series.

The steric orientation of the methyl groups in the quinolizidine alkaloids of the yellow lily has been found with the aid of the benzene-induced shift of the NMR signal due to these groups[100,101]. The dependence of the shift of the signal of the methyl group induced by an aromatic solvent on the latter's position in the bicyclic system was studied recently[102] for nine monomethylquinolizidines. The conclusions reached in the above studies[100,101] are consistent with the observed empirical correlation[102] and the latter can evidently be useful for the determination of the orientations of the methyl or methylene groups in other quinolizidine derivatives.

New possibilities for the investigation of the stereochemistry of 1-azabicyclic systems arose owing to the introduction of ^{13}C NMR spectroscopy. The ^{13}C chemical shifts in quinolizidine (I),[103-105] indolizidine (II),[104] and pyrrolizidine (III)[106] were determined, which constitutes the essential starting point in the investigation of derivatives of compounds (I)–(III) by ^{13}C NMR.

On the basis of spectroscopic data for quinolizidine (I) and methyldecalins with the *trans*-junction, LaLonde and coworkers interpreted the ^{13}C NMR spectra of eight monomethylquinolizidines[105] and isomeric 3-methyl-3-methylthiomethylquinolizidines.[107] The results were used in the analysis of the ^{13}C NMR spectra of nine *Nuphar* alkaloids[107]. The determination of the chemical shifts in (I), the epimeric 1-hydroxymethylquinolizidines, and their benzoates assisted in the interpretation of the ^{13}C NMR spectra and the determination of the steric structures of 1,9-disubstituted quinolizidines[92].

The consideration of the ^{13}C NMR spectra of lactams of the sparteine series was preceded by a study of the spectra of 3-oxo- and 1-methyl-3-oxoquinolizidines.[108] The signals of the ^{13}C nuclei in 9-hydroxymethyl-3-methyl- and 7-hydroxymethyl-1-methyl-*cis*-2,10-*H*-2-hydroxyquinolizidines and azabenzenecarboxylate esters of 3-hydroxyquinolizidines were assigned in the same investigation[108].

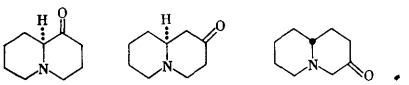
The results obtained can serve as a basis for the study of the steric structures of new and more complex compounds, particularly natural products. The relevant examples have been described in a number of communications[92,107-109].

7. X-Ray Diffraction Analysis

In connection with the automation of X-ray diffraction analysis[110], on the one hand, and the possibility of preparing crystalline salts of quinolizidine, indolizidine, and pyrrolizidine bases, on the other, this method is one of the most promising for the determination of the steric structures and, particularly, the absolute configurations of the derivatives of the 1-azabicyclic compounds under consideration. Studies on the application of X-ray diffraction analysis in the determination of the configurations of salt-like quinolizidines, indolizidines, and pyrrolizidines are reviewed in Section IV.

8. Other Methods

The study of the circular dichroism of optically active (–)-1-oxoquinolizidine (XCVI), (+)-2-oxoquinolizidine (XCVII), and (–)-3-oxoquinolizidine (XCVIII) made it possible to determine the absolute configurations of these aminoketones[111].



(XCVI) (XCVII) (XCVIII)

The identity of the configurations at the $C_{(4)}$ atom in the quinolizidine alkaloids vertaline and decaline follows from a comparison of their optical rotatory dispersion and circular dichroism curves[70]. The circular dichroism data have been used in the determination of the structures of 6-hydroxythiobinupharidine, 6-hydroxythionuphlutine,[112] and the quinolizidine mono-*gem*-aminals from *Nuphar luteum*.[113]

Culvenor and coworkers studied the circular dichroism of a series of simple pyrrolizidine bases and certain pyrrolizidine alkaloids. The sign and magnitude of the Cotton effect for both the simplest bases and open-chain ester alkaloids depend on the configuration at $C_{(8)}$, on the positions of the substituents, and on the degree of saturation of the bicyclic system[114]. Saturated pyrrolizidines with one substituent in the 1-position, namely heliotridane, the enantiomer of isoretronecanol, 1β,2β-epoxy-1α-hydroxymethyl-8α-pyrrolizidine, and 1α,2α-epoxy-1β-hydroxymethyl-8α-pyrrolizidine exhibit a negative Cotton effect. Retronecanol, which has a 7β-hydroxy-group, in contrast to the previous compounds, and the unsaturated bases supinidine, deoxyretronecine, retronecine, and heliotridine exhibit a positive Cotton effect. The magnitude of the effect for the last two compounds apparently depends on the configuration at $C_{(7)}$.[114]

The applicability of the octant rule to the determination of the absolute configurations of α-aminoketones of the quinolizidine, indolizidine, and pyrrolizidine series has been examined[115].

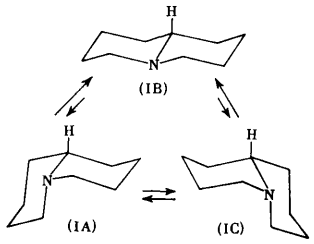
Slight differences have been observed between the mass spectra of lupinine and epilupinine[116] and between those of the four isomeric 4-phenyl-1-quinolizidinols.[117] A mass-spectrometric study of 6-hydroxythiobinupharidine, 6-hydroxythionuphlutine *B*, and 6'-hydroxythionuphlutine *L* assisted in the determination of the configuration at $C_{(6)}$ in these compounds[112]. The mass spectra of the isomeric 7-hydroxy-1-hydroxymethylpyrrolizidines (platynecine, dihydroxyheliotridane, hastanecine, and turneforcidine) are similar, but differ from the spectra of 2-hydroxy-1-hydroxymethylpyrrolizidines[59]. Using mass spectra, it is difficult to reach a conclusion about the orientation of the hydroxymethyl group in the isomeric 1-hydroxymethylpyrrolizidines (trachelanthamidine and lindelofidine).[118] However, it has been suggested[118] that, in a mass spectrometric study of pyrrolizidines with bulky substituents, it might be possible to determine their steric positions.

The dipole moment method has not so far been used widely in the determination of the configurations of quinolizidines, indolizidines and pyrrolizidines. Satisfactory results have been obtained by this method in the stereochemical study of 1- and 3-hydroxymethylquinolizidines[60,119] and also 3-(4-chlorobenzyl)quinolizidines.[60] The isomers were assigned by a qualitative interpretation of the vector scheme for each pair of epimers, which makes it possible

to predict higher dipole moments for compounds with the *cis*-configurations. The equatorial location has been attributed to the hydroxyethyl group of 6-hydroxyethyl-3,9-dimethylquinolizidine on the basis of its dipole moment[120].

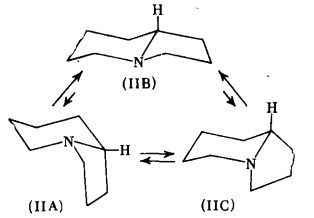
III. CONFORMATIONAL ANALYSIS OF THE BASES

The central problem of the conformational analysis of quinolizidines is the ratio of forms having *cis*- and *trans*-junctions, which can undergo interconversions by virtue of the inversion of the nitrogen atom. For quinolizidine itself, these ratios are reflected in the following scheme:



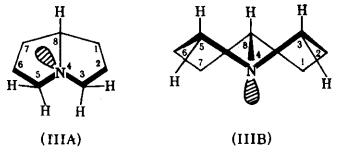
The flexible forms (IA) and (IC) with the *cis*-junction are interconvertible enantiomers and henceforth will be treated as a single conformation (IA). The conformations with one or two rings in the boat form are not discussed because they are known to be unfavourable owing to non-bonding interactions. However, among certain quinolizidine derivatives compounds are encountered where the boat conformation of one of the rings is possible.

Indolizidine (II) also has two conformations (IIA) and (IIC) with a *cis*-junction and a conformation (IIB) with a *trans*-junction:



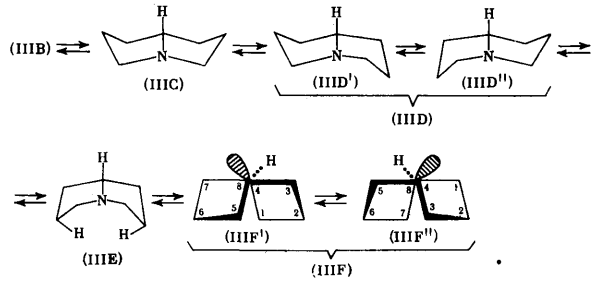
It is readily seen that, in contrast to the quinolizidine conformers (IA) and (IC), the *cis*-conformers (IIA) and (IIC) are energetically non-equivalent.

Of the two forms of pyrrolizidine (IIIA) and (IIIB), the (IIIA) form with a *cis*-junction was chosen because, in contrast to (IIIB), it is free from appreciable strain[121].



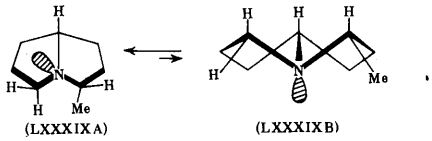
Subsequently the idea of a *cis*-junction between the rings in pyrrolizidines was adopted in many investigations[30,72,122-124]. However, it was shown[125] that in certain intramolecular quaternisation reactions there is a possibility of the formation of quaternary salts with a fixed pyrrolizidine skeleton having a *trans*-junction.

trans-Fused (IIIB), open (IIIC), half-folded (IIID)†, and folded (IIIE) conformations have been postulated[126] for pyrrolizidine (III):



As a result of unfavourable non-bonding interactions, the conformation (IIIE) resembles the cyclohexane boat form and, by analogy with cyclohexane and derivatives of *cis*-bicyclo[3,3,0]octane,[127] it can be assumed that, in an "endeavour" to weaken non-bonding *trans*-2-*H*...*trans*-6-*H* interactions, the (IIIE) conformation undergoes a twisting deformation. This results in two enantiomeric twisted conformations (IIIF′) and (IIIF″) (the five-membered ring exists in the half-chair form) and these acquire some angular strain, which relates them to the twist-form of cyclohexane. The (IIIC) and (IIID) conformations are free from strong non-bonding interactions and angular strain and their enthalpies are apparently similar, which is a feature resembling the insignificant difference between the energies ($\Delta H \simeq 0.1$ kcal mole^{-1}) of the C_{2v} (open) and C_s (half-folded) conformations of *cis*-bicyclo[3,3,0]-octane.[128]

The change in the conformational equilibrium between the (LXXXIXA) and (LXXXIXB) forms of the free pyrrolizidine base with *cis*-‡ and *trans*-junctions under the influence of a change in temperature has been observed[126] by NMR in relation to (LXXXIX):

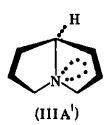


Analogous conformational effects may be expected also in those cases where a hydroxymethyl[18,19] or a β-hydroxyethyl group is introduced instead of the methyl group[20].

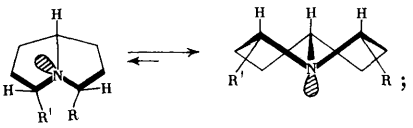
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†Each pair of enantiomeric conformations (IIID′), (IIID″), and (IIIF′), (IIIF″), will be treated for simplicity as (IIID) and (IIIF) forms.

‡In those cases where the *cis*-fused conformations are not distinguished, their families are nevertheless designated by schematic diagrams of type (IIIA) or (IIIA′):



Evidently the fraction of the *trans*-fused form can be significantly increased by intensifying the non-bonding interactions in the *cis*-fused conformations of pyrrolizidines. This was achieved in two ways: by introducing a t-butyl group instead of the *trans*-3-*H* atom and by introducing two methyl groups instead of the *trans*-3-*H* and *trans*-5-*H* atoms in the pyrrolizidine molecule. The non-bonding interactions in the *cis*-fused conformations (XCIXA) and (XCIIA) of pyrrolizidines (XCIX) [28] and (XCII) [17] are so intense that the compounds exist mainly in the *trans*-fused forms (XCIXB) and (XCIIB) despite the marked angular strain in them [17,28,79]:



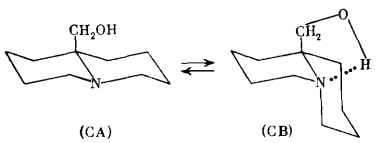
(XCIXA), R = t-Bu, R'=H; (XCIXB), R= t-Bu, -Bu, R'=H;
(XCIIA), R = R' = Me; (XCII), R = R' = Me .

The idea of an appreciable contribution by the *trans*-fused form to the equilibrium mixture of the conformations of compound (XCV) has been confirmed by experiments on its oxidative dehydrogenation by mercury acetate [129].

1. Determination of the Preferred Conformations. A Qualitative Approach

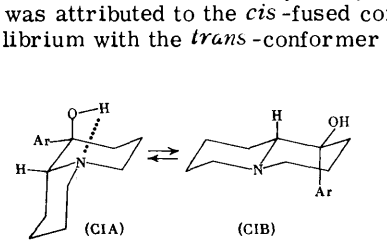
(a). Vibrational spectroscopy. The application of infrared spectroscopy in the conformational analysis of quinolizidines and indolizidines has been described in detail in a review [9]. In the range 2700–2800 cm^{-1} (in the region of the stretching vibration frequencies of the hydroxy-group) "spectroscopy" proved to be particularly valuable in the determination of the preferred conformations of alcohols of the quinolizidines [9,56,74,84,100,117] and indolizidine [9,83,84] series.

In contrast to other simplest quinolizidine alcohols [9], 10-hydroxymethylquinolizidine (C) in a dilute solution exhibits absorption bands due to both free and bound hydroxy-groups, which indicates the existence of an equilibrium between conformations (CA) and (CB) with *trans*- and *cis*-junctions respectively [130]:



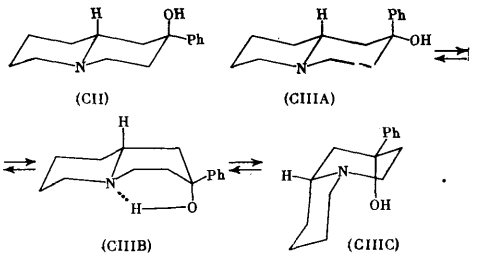
(CA) (CB)

The appreciable absorption typical of intramolecular hydrogen bonds in the spectra of 1-aryl-1-hydroxyquinolizidines (CI) was attributed to the *cis*-fused conformation (CIA) in equilibrium with the *trans*-conformer (CIB) [56];



(CIA) (CIB)

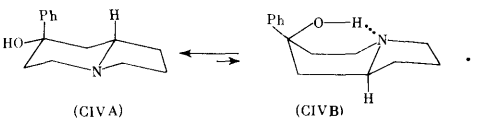
The structures of 2-hydroxy-2-phenylquinolizidines (CII) and (CIII) [84,131] were examined almost simultaneously and independently:



(CII) (CIIIA) (CIIIB) (CIIIC)

The spectrum of isomer (CII) in dilute solutions has only one peak corresponding to the free hydroxyl, while the spectrum of its epimer (CIII) has a weak absorption band characteristic of the vibrations of an intramolecular hydrogen bond. This observation enabled the authors [84,131] to conclude that the equilibrium mixture contains, together with form (CIIIA), also the conformation (CIIIB), in which the six-membered ring with substituents is in the boat form. The (CIIIC) conformation was not discussed [84,131], although it can apparently make a contribution, by analogy with (CIA).

Similarly the spectrum of 7-hydroxy-7-phenylindolizidine (CIV) in dilute solutions has absorption bands due to free [(CIVA) conformation] and bound hydroxyls [(CIVB) conformation with the six-membered ring in the boat form] [84]:



(CIVA) (CIVB)

Vibrational spectroscopy is in essence only just beginning to be applied in the study of the conformations of pyrrolizidines. Comparison of the infrared and Raman spectra of pyrrolizidine and *cis*-bicyclo[3,3,0]octane and also the results of the calculation of the frequencies and modes of the normal vibrations of these compounds show that, under the usual conditions, pyrrolizidine is a mixture of mainly two conformations—the open conformation (IIIC) and the half-folded conformation (IIID). [132,133]

In the region of the skeletal-deformation vibrations the Raman spectra of the strained pyrrolizidines (XCII) and (XCIX) have a smaller number of frequencies than the spectra of the corresponding isomers with a *cis*-junction between the rings, which is interpreted as a consequence of the preferential *trans*-junction in the (XCIIB) and (XCIXB) states [28,133,134]. From the standpoint of the study of the region of applicability of the Bohlmann correlation, discussed in a review [9], it is of interest to observe the absorption in the range 2700–2800 cm^{-1} characteristic of the strained preferentially *trans*-fused pyrrolizidines (XCII) and (XCIX). [79,134] The contribution of the $C_{(8)}$–H bond to the effect was demonstrated by introducing deuterium instead of hydrogen in the 8-position [79].

(b) NMR spectroscopy. The chemical shifts of the protons attached to the α-carbon atoms and the gemina (α-methylene group) and vicinal spin–spin coupling constants for protons are used as criteria for the determination of the preferential type of junction between the rings in quinolizidines, indolizidines, and pyrrolizidines.

The spectra of *trans*-fused 1-azabicyclic compounds contain the signal due to the angular proton at a higher field than the corresponding *cis*-fused bases[9,126,135]. Measurement of the chemical shifts of the signals due to the protons attached to the bridgehead carbon atoms serves as a fairly general procedure for the investigation of the conformations of 1-azabicyclic compounds[57,136,138]. Under these conditions, a comparison of the chemical shifts obtained for the test base and its isomer or another compound used as a standard (with a definite type of junction between the rings) is as a rule required. In certain instances[17,28,92,139] difficulties are encountered owing to the localisation of the angular proton multiplet in the ^{1}H NMR spectra.

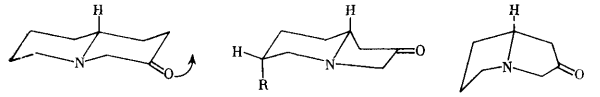
The virtual invariance of the pyrrolizidine spectrum in the temperature range from −17° to +190° leads to the conclusion that the compound is largely if not entirely in the *cis*-fused conformation (IIIA).[126] The ^{1}H NMR spectrum of compound (LXXXIX) exhibits, in contrast to the spectra of its epimer (LXXXVIII) and pyrrolizidine (III), a distinct dependence of the chemical shifts of a number of signals, which reflects a change in the equilibrium between the *cis*-fused and *trans*-fused forms [(LXXXIXA) and (LXXXIXB)] respectively. The upfield displacement of the 8-H proton signal with increase of temperature serves as a criterion indicating an increase of the content of the *trans*-fused conformation (LXXXIXB).[126] The similarity of the chemical shifts of the 8-H protons in pyrrolizidine (3.33 p.p.m.) and in the epimers (LXXXVIII) (3.45 p.p.m.) and (LXXXIX) (3.31 p.p.m.) as well as the results of measurements of the temperature variation show that the *cis*-fused conformations of compound (LXXXIX) predominate[126].

When the methyl group in (LXXXIX) is replaced by the t-butyl group as in (XCIX), a significant diamagnetic shift of the 8-H proton signal is observed ($\delta \leqslant 2.95$ p.p.m.).[28] The H-8 proton resonates at a higher field also in compound (XCII) ($\delta < 3$ p.p.m.).[17] The preferentially *trans*-fused conformations (XCIXB) and (XCIIB) have been attributed to these pyrrolizidine homologues[17,28].

The position of the signal due to the 4-H proton in 4-arylquinolizidines serves as a diagnostic characteristic of the *cis*- or *trans*-fused conformation—in the former the signal is at a lower field than in the latter[58,69,70,135,140,141]. Comparison of the ranges of the chemical shifts for *cis*- or *trans*-fused 4-arylquinolizidines[69] shows that they can overlap for different groups of compounds, but, according to the literature, the determination of the preferential conformations of epimers is fairly reliable.

The preferential *trans*-junction between the rings in lupinine is evident from the chemical shifts of the axial and equatorial protons at $C_{(4)}$ and $C_{(6)}$.[142]

The amount of information about the geminal spin–spin coupling constants in the quinolizidine, indolizidine, and pyrrolizidine series is still relatively limited[143,144] and the influence of different types of junction between the rings on J_{gem} is apparently small[145] as long as the CH_2 group is not located between nitrogen and another heteroatom[9] or a carbonyl group[76]. The contribution of π electrons ($\Delta J = -3.2$ Hz) to $^2J_4$-CH_2 was determined by comparing the geminal constants for the 4-CH_2 group in 3-oxoquinolizidine (CV) and [3D_2]quinolizidine, whence it was found that the ring with the carbonyl group is deformed; the carbonyl group is slightly rotated towards the 10-H atom owing to the dipole repulsion interaction between it and the nitrogen atom[76]:



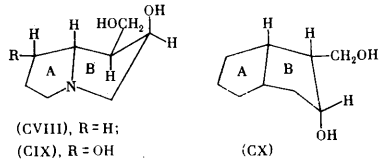
(CV) (CVI), R = Me; (CVII), R = Et (XXXVA)

Having investigated the geminal constants for the 3-CH_2 group and in certain cases the 5-CH_2 group in 3-, 5-, 6-, 7-, and 8-alkyl-2-oxoindolizidines, Cahill and Crabb[76] concluded that they exist in *cis*-fused conformations. The problem of the contribution of the *cis*-fused forms was studied specially in relation to compounds (CVI) and (CVII). The conformational homogeneity of compounds (CVI) and (CVII) was inferred on the basis of the constant $^2J_5$-CH_2 = −11.0 Hz. The contributions of the lone electron pair of the nitrogen atom and the π electrons of the carbonyl group to the constant $^2J_3$-CH_2 for 3-, 5-, 6-, 7-, and 8-alkyl-2-oxoindolizidines were separated. According to the last contribution (−6.7 Hz), the $C_{(1)}$, $C_{(2)}$, $C_{(3)}$, and N atoms are located in the same plane[76].

The very low geminal constant J_3-CH_2 = −18.5 Hz in compound (XXXV) was attributed to the bisector location of the carbonyl group in relation to the 3-CH_2 group and the conformation with an *endo*-puckered N, $C_{(5)}$, $C_{(6)}$, $C_{(7)}$, $C_{(8)}$ ring (XXXVA).[76]

The splitting of the signal due to the angular proton in benzo[*a*]quinolizidine, indolo[*a*]quinolizidine,[137] and dibenzo[*a*,*g*]quinolizidines[136,138] was used to choose one of the possible conformations with a *cis*-junction between the rings.

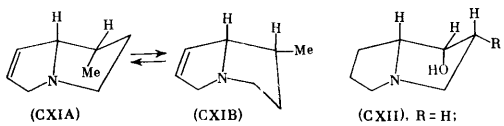
In the study of *cis*-fused conformations of pyrrolizidines considerable progress has been achieved as a result of the investigation of substituted and partly unsaturated bases, from the ^{1}H NMR spectra of which the spin–spin coupling constants for the vicinal protons were determined and their dependence on the geometry was employed. Thus it was found from the values of $J_{H,H}$ for the B rings in compounds (CVIII)–(CX) that the first two compounds[59,98] have conformations with an *exo*-puckered B ring, while the last compound[59] has a conformation with an *endo*-puckered ring.



(CVIII), R = H; (CIX), R = OH (CX)

In all three cases the conformation of the B ring is apparently dictated by the preferential pseudoequatorial orientation of the hydroxymethyl group in the 1-position; the conformation of the A ring has not been discussed.

Detailed analysis of the ^{1}H NMR spectrum of heliotridene (CXI) showed that the free base in solution in $CDCl_3$ consists of an equilibrium mixture of two conformations, (CXIA) and (CXIB), in proportions of approximately 1 : 1[97]:

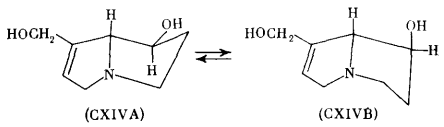


(CXIA) (CXIB) (CXII), R = H; (CXIII), R = OH

The angle of pucker§ of the saturated ring in conformations (CXIA) and (CXIB) is 45°.

The retronecine molecules have the (CXII) conformation with an *exo*-pucker of the saturated ring (angle of deflection 40°) and a pseudoaxial 7-OH hydroxyl; furthermore, they undergo additional twisting of the bicyclic system about the axis passing through the $C_{(2)}$ and $C_{(6)}$ atoms in a direction such that the 3β-H atom tends to occupy a pseudoequatorial position and the saturated ring approaches the half-chair form[96]. Crotanecine has a similar form (CXIII) in aqueous solution[99].

Agreement between the experimental and calculated vicinal spin–spin coupling constants for heliotridine (CXIV) is achieved if it is assumed that the compound is an equilibrium mixture of the (CXIVA) and (CXIVB) conformations with angles of pucker of the saturated ring equal to 40° [96]:



(CXIVA) (CXIVB)

The application of modified Karplus equations, taking into account the influence of nitrogen and oxygen atoms in (CXIV), made it possible to obtain a very satisfactory agreement between the calculated and experimental values of $^3J_{H,H}$ for the (CXIVA) : (CXIVB) = 35 : 65 mixture[97].

On the basis of the results of the calculation of the geometries of the molecules with the aid of a mechanical model and analysis of the geminal, vicinal, and allyl spin–spin coupling constants, Van Binst et al.[146] concluded that the geometry of the bicyclic system in compounds (CXV)–(CXVII) is virtually the same—the nitrogen is in the sp^2-hybridised state and the bicyclic system has a rigid highly strained (17.2 kcal mole^{-1}) skeleton.

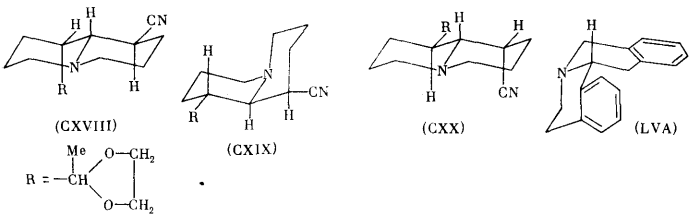


(CXV), X=Y=O;
(CXVI), X=Y=CHCN;
(CXVII), X=O, Y=$CHCO_2Et$.

Whereas the identification of the signals in the ^1H NMR spectra which cannot be interpreted initially sometimes constitutes a very complex problem[92,139], ^{13}C NMR spectra are frequently fairly simple. In the determination of the type of junction between the rings in quinolizidine, lupinine, epilupinine, their benzoate esters, and the isomeric compounds (CXVIII)–(CXX) the positions of the signals due to $C_{(4)}$, $C_{(6)}$, and $C_{(10)}$ are instructive. The shift of the signal due to the $C_{(4)}$ and $C_{(6)}$ nuclei in the *trans*-fused isomers (CXVIII) and (CXX) is approximately constant (57 p.p.m.). On the other hand, in the *cis*-fused compound (CXIX) the signals due to the $C_{(4)}$ and $C_{(6)}$ nuclei are significantly displaced in the upfield direction. According to Wenkert et al.[92], the location of the $C_{(4)}$ signal of this isomer at an anomously high field (47.1 p.p.m.) is a consequence of two γ-effects generated by the carbon atoms of a neighbouring ring, i.e. caused by 1.3-diaxial non-bonding interactions of one of the 4-H atoms with the hydrogen atoms of the neighbouring ring.

The chemical shift of the $C_{(10)}$ nucleus in compound (CXIX) is approximately 6 p.p.m. higher than in the *trans*-fused bases (CXVIII) and (CXX).[92,104] This finding can be given an explanation analogous to that quoted above for the $C_{(4)}$ and $C_{(6)}$ nuclei.

The stereochemistry of tetrahydroprotoberberines, which are derivatives of dibenzo[*a*,*g*]quinolizidine (LV), can be readily inferred from the chemical shifts of the $C_{(6)}$ nuclei: compounds with a *cis*-junction between the B and C rings have chemical shifts of 48.3 p.p.m. or less, while compounds with a *trans*-junction give rise to signals at lower a field (51.4 ± 0.1 p.p.m.). The position of the signal due to the angular $C_{(13a)}$ atom depends just as clearly on the nature of the junction between the rings[136,147]. Tetrahydroprotoberberines with a methoxy-group at $C_{(1)}$ assume preferentially the *cis*-fused conformation of type (LVA) in which non-bonding interactions between the methoxy-group and 13-H, which occur in the *trans*-fused and the second *cis*-fused conformations[136,147], are eliminated[136,147]:



(CXVIII) (CXIX) (CXX) (LVA)

The chemical shift of the $C_{(6)}$ atom in capaurimine is 49.3 p.p.m. and the compound consists of a mixture of *cis*- and *trans*-fused conformations[36].

The symmetry and stereochemistry of the isomeric perhydropyrido[2,1,6-*de*]quinolizidines have been inferred from the number of signals in their ^{13}C NMR spectra[109].

The similarity of the conformations of the strained pyrrolizidines (XCII) and (XCIX) is clearly seen from their ^{13}C NMR spectra. The signals due to the $C_{(8)}$ nuclei in these compounds are in the range 70.1–72.7 p.p.m., while other unstrained *cis*-fused pyrrolizidines are characterised by shifts of the $C_{(8)}$ signals in the range 64–66.6 p.p.m.[106]

Other methods. The rate of methylation of alkaloids of the yohimbine and heteroyohimbine series is satisfactorily correlated with their stereochemistry[66,67]. Yohimbine reacts with methyl iodide more slowly approximately by two orders of magnitude than does pseudoyohimbine, which, in contrast to the former compound, has a *cis*-fused quinolizidine fragment and a sterically more accessible nitrogen atom[65].

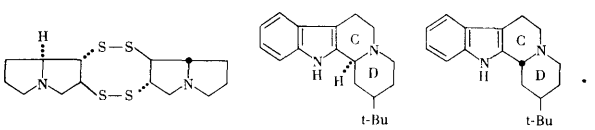
The 1-H and 13-H atoms, which are in the *cis*-positions relative to 13a-H, are closer together in dibenzoquinolizidine (LV). The introduction of a more bulky substituent in place of one of these atoms gives rise to intense non-bonding interactions, which forces the molecule to assume the conformation with a *cis*-junction between the B and C rings. Study of the kinetics of the quaternisation of dibenzoquinolizidine derivatives (tetrahydroprotoberberines) served as a means for determining the conformations of these compounds in solution. It has been shown in this way that capaurine and capaurimine exist in solution in conformations with a *cis*-junction between the B and C rings[65]. Vertine and vertaline, which have a *cis*-fused quinolizidine fragment, react with methyl iodide much faster than their epimers lythrine and decaline, in which the quinolizidine rings are *trans*-fused[69,70]. The relative inertness of compound (XCII) compared with its isomers (XC) and (XCI) in the reaction with n-propyl iodide can be

§The angle between the planes passing through the $C_{(1)}$, $C_{(3)}$, N, and $C_{(8)}$ atoms, on the one hand, and through the $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ atoms, on the other[97].

accounted for by the considerable contribution of the *trans*-fused form (XCIIB) (see the beginning of this section) to the equilibrium mixture of its conformations[17].

According to X-ray diffraction data, the free base of capaurimine *p*-bromobenzoate has a *cis*-junction between the B and C rings in the crystalline state[148]. In crystalline cassipourine (CXXI) the pyrrolizidine rings have a half-folded conformation of type (IIID), the angle between the planes passing through the $C_{(1)}$, $C_{(3)}$, N, and $C_{(8)}$ atoms, on the one hand, and the $C_{(5)}$, $C_{(7)}$, $C_{(8)}$, and N atoms, on the other, is 123°.[149]

A difference has been observed between the mass spectra of compounds (CXXII) and (CXXIII). On electron impact, the epimer (CXXII) loses the oxygen at $C_{(12)}$ much more readily than the epimer (CXXIII), since the 12-H atom and the lone electron pair of the nitrogen atom are in the *trans*-diaxial positions and there is a *trans*-junction between the C and D rings only in the former epimer[150]:



(CXXI) (CXXII) (CXXIII)

The dependence of the mass spectra of the stereoisomeric alkaloids matrine, allomatrine, isosophoridine, and sophoridine on the steric structure has been demonstrated and studies on the mass spectrometry of these and other quinolizidine alkaloids have been reviewed[151].

By studying the ultraviolet spectra of compounds (XCVI)–(XCVIII), Mason et al.[111] found that the carbonyl group in compounds (XCVI) and (XCVIII) absorbs more intensely than that in (XVII) and other carbocyclic ketones owing to the interaction of the carbonyl π orbitals and the lone pair of electrons of the nitrogen. Such interaction can occur only in *trans*-fused forms of compounds (XCVI) and (XCVIII), whence it is concluded that this conformation is preferred[111].

The type of junction between the rings in pyrrolizidines has a fairly marked influence on their basicity. While the *cis*-fused compounds (I), (LXXXVIII), (LXXXIX), heliotridane (pK_a = 11.48),[152] (XC), and (XCI) are some of the strongest saturated bases with a tertiary nitrogen atom (for the values of pK_a see Section II, subsection 4), the predominantly *trans*-fused (XCII) has a relatively low pK_a = 10.28,[87] close to the pK_a values of related typically *trans*-fused 1-azabicyclic compounds, such as quinolizidine (10.19)[64] and indolizidine (10.15).[86]

The comparatively high basicity of *cis*-fused pyrrolizidines[86,123,152,153] can be explained by their stereochemical characteristic feature consisting in the steric accessibility of the nitrogen[123,153] and a geometry which is unfavourable for the delocalisation of the lone electron pair of the nitrogen[86]. This property of the pyrrolizidine *cis*-fused bicyclic system can be readily discovered by comparing the basicities of quinolizidine, indolizidine, and pyrrolizidine alcohols with the hydroxy-group in the 2-position relative to the nitrogen, which do not form intramolecular hydrogen bonds (Table 1). Thus one may reach a conclusion about the sequence of increasing basicities of unsubstituted bicyclic systems. Quinolizidine and indolizidine are virtually equivalent as bases, whereas pyrrolizidine is significantly stronger. This conclusion is confirmed by recent direct observations for the free bases (I)–(III),[86] whose pK_a values are 10.19,[64] 10.15, and 11.68[86] respectively. In aqueous solution base (III) differs in strength from compounds (I) and (II) by more than an order of magnitude.

Table 1. The basicities of certain quinolizidine, indolizidine, and pyrrolizidine alcohols.

Compound	pK_a	Refs	Compound	pK_a	Refs
(LIX)	8.73	38	(LXXI)	8.33	25
(LXI)	8.60	38	(XXXIV)	10.35	30
(LXVII)	8.59	30	(XLVIII)	10.25	30
(LXIX)	8.82	30	(XXXVI)	10.25	30

2. Quantitative Results

Certain results of the quantitative study of the *cis–trans* interconversion of quinolizidine and indolizidine have been published[9]. We arranged systematically and compiled in Table 2 data for the conformational equilibria involving both the bases (I)–(III) themselves and their derivatives.

The conflicting results obtained in the determination of the thermodynamic parameters of the *cis–trans* interconversion in quinolizidine led us to calculate the enthalpy of this process in two independent ways[159]. The calculation was based on the enthalpy of the *cis–trans* isomerisation of decalines. Ultimately, as a result of this treatment[159], the energy of the additional stabilisation of the *trans*-fused form of quinolizidine relative to *trans*-decaline was obtained from data for piperidine and calculated from the results of the determination of the energies of hydrogen bonds in the quinolizidine–phenol and quinuclidine–phenol systems[159]. It was shown[158,162] that at least in the gas phase the values of ΔG°_{25} for the *cis–trans* interconversions in quinolizidine and indolizidine differ more significantly than is believed in the literature[157,163].

At the present time there have been no rigorous determinations of the thermodynamic parameters of the *cis–trans* interconversion in pyrrolizidines. It has been suggested[126] that there is a difference between the heat contents of the *cis*- and *trans*-fused pyrrolizidines, which is close to that described for the isomeric *cis*- and *trans*-bicyclo[3,3,0]octanes (6.0 kcal mole^{-1}).[164]

Assuming that an increase of the content of the *trans*-fused form of pyrrolizidine to 5% on heating its vapour from 20° to 300°C would be observed from the appearance of Bohlmann bands in the range 2700–2800 cm^{-1} and having failed to observe this effect with increase of temperature, Skvortsov et al.[158] calculated $\Delta H < -3.4$ kcal mole^{-1} for the *trans–cis* conversion in pyrrolizidine.[158]

IV. THE CONFIGURATIONS AND CONFORMATIONS OF THE BASES AND QUATERNARY SALTS PROTONATED AT THE NITROGEN ATOM

The quinolizidinium cation in trifluoroacetic acid has a *trans*-junction between the rings; its ^1H[165] and ^{13}C[103] NMR spectra have been described. A *trans*-junction

Table 2. Quantitative data for the conformational equilibria in quinolizidines, indolizidines, and pyrrolizidines.

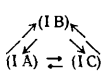
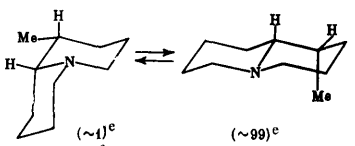
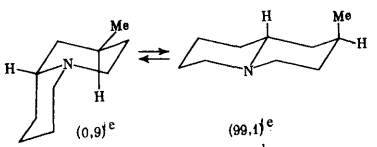
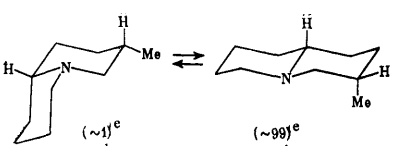
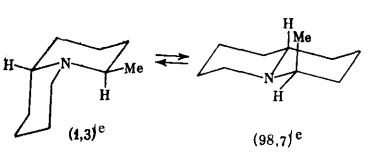
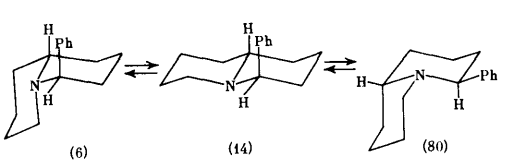
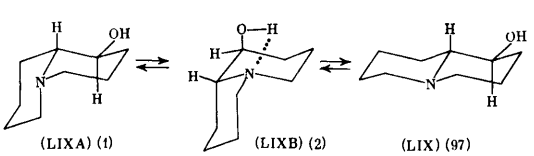
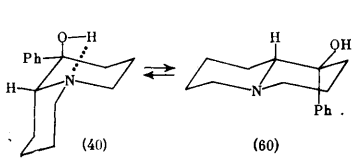
Equilibrium conformation[a] (content in % at 20–33°)	Method[m]	$-\Delta H°$, kcal mole^{-1}	$-\Delta G^{\circ}_{20-33°}$, kcal mole^{-1}	References
1	2	3	4	5
 (IA) ⇄ (IC)	*A*	1.9	—	154
	A	—	4.6	155
	—	2.6		156
	B	—	4.4	64
	C	—	2.6	157
	C	>3.4	—	158
	A, C	—	2.0±0.35[b]	117
	A	3.3[c]	—	
		3.7; 4.3[d]	—	159
 (~1)[e] (4)[f] (~99)[e] (96)[f]	*B*	—	—	64
 (0,9)[e] (1)[b] (99,1)[e] (99)[b]	B	—	—	64
 (~1)[e] (7)[b] (~99)[e] (93)[b]	*B*	—	—	64
 (1,3)[e] (98,7)[e]	*B*	—	—	64
 (6) (14) (80)	*A, C*	—	—	117
 (LIXA) (1) (LIXB) (2) (LIX) (97)	*C*	—	2.1[g]	157
 (40) (60)	*C*	—	—	157

Table 2 (cont'd.).

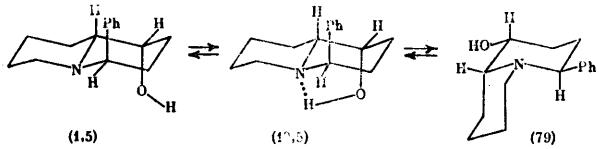
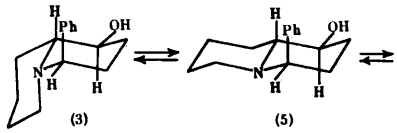
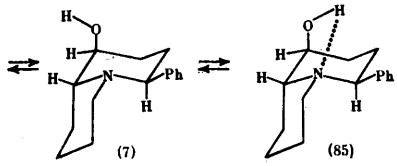
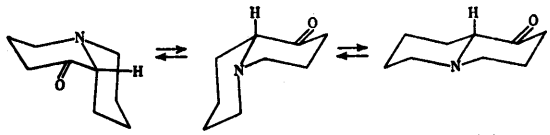
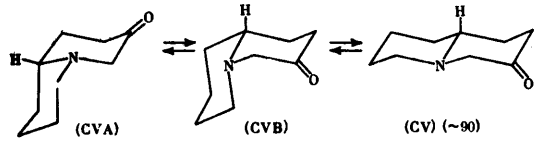
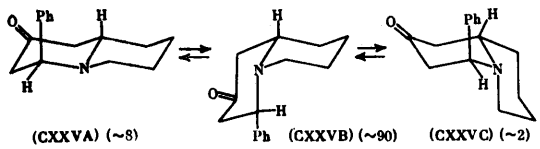
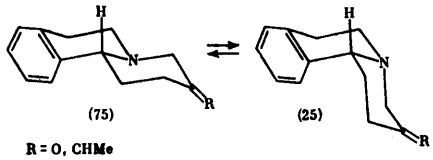
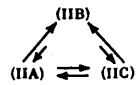
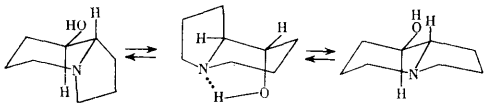
Equilibrium conformation[a] (content in % at 20–33°)	Method[m]	$-\Delta H°$, kcal mole^{-1}	$-\Delta G°_{20-33°}$, kcal mole^{-1}	References
1	2	3	4	5
 (1,5) (1?,5) (79)	*C*	—	—	117
 (3) (5)	*C*	—	—	117
 (7) (85)				
 (CXXIVA) (3) (CXXIVB) (~7) (CXXIVC) (~90)	*D*	1.95[h]	—	111
 (CVA) (CVB) (CV) (~90)	*D*	2[i]	—	111
 (CXXVA) (~8) Ph (CXXVB) (~90) (CXXVC) (~2)	*A*	—	1.5[j] 2.3[k]	140
 (75) (25) R = O, CHMe	*E*	—	—	160
 (IIB) (IIA) (IIC)	*A* *B* *C*	0.3 0.9 —	— — 2.4	154 161 157

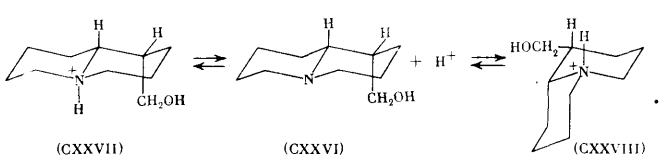
Table 2 (cont'd.).

Equilibrium conformation[a] (content in % at 22-33°)	Method[m]	$-\Delta H^{\circ}$, kcal mole^{-1}	$-\Delta G^{\circ}_{20-33^{\circ}}$, kcal mole^{-1}	References
1	2	3	4	5
 (LXXIA) (1) (LXXIB) (3) (LXXI) (96)	C	—	1.9[l]	157
(III B) ⇄ (III A)	C A	≥3.4 <6	— —	158 126

[a]Conformations whose content is close to zero are not taken into consideration.
[b]The value is applicable only to calculations for the series of derivatives of *trans*-4,10-*H*-4-phenylquinolizidine.[117]
[c]For the liquid phase.
[d]For the gas phase.
[e]In solution in MeCN.
[f]In solution in MeOH.
[g]For the equilibrium(LIXA) + (LIXB) ⇌ (LIX).
[h]For the equilibrium (CXXIVA) + (CXXIVB) ⇌ (CXXIVC).
[i]For the equilibrium (CVA) + (CVB) ⇌ (CV).
[j]For the equilibrium (CXXVA) ⇌ (CXXVB).
[k]For the equilibrium (CXXVC) ⇌ (CXXVB).
[l]For the equilibrium (LXXIA) + (LXXIB) ⇌ (LXXI).
[m]*A* = conformational analysis, *B* = kinetic analysis, *C* = infrared spectroscopy, *D* = chiro-optical analysis, and *E* = NMR spectroscopy.

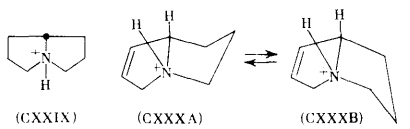
between the rings has been attributed to protonated quinolizidine, *trans*-1,10-*H*-1-methylquinolizidine, 2-methylquinolizidine, 3-methylquinolizidine, and *cis*-4,10-*H*-4-methylquinolizidine in aqueous solution[12], i.e. the cations have the same configuration as the conformations of the corresponding free bases. Two doublets due to the methyl group were observed for *cis*-1,10-*H*-1-methylquinolizidine. This was explained by the tautomeric equilibrium between approximately equal amounts of the *trans*- and *cis*-fused forms of the cation[12]. According to the authors[12], the *trans*-4,10-*H*-4-methylquinolizidinium cation has a *cis*-junction between the rings.

Whereas according to NMR spectra protonated epilupinine exists in the *trans*-fused form[166], the protonation of lupinine (CXXVI) gives rise to cations with a *cis*-junction [compound (CXXVII)] and a *trans*-junction [compound (CXXVIII)] junction between the rings, which can undergo interconversions in solution; the equilibrium position depends on the concentration, the pH, and temperature[166]:


(CXXVII) (CXXVI) (CXXVIII)

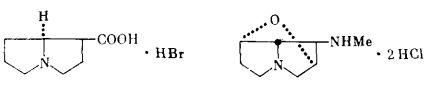
Protonated 1-hydroxy-7-methyl- and 1-hydroxy-1,7-dimethyl-quinolizidines in trifluoroacetic acid retain the *trans*-fused form of the free bases according to ^{1}H NMR spectra[167]. Protonation of 5,7-dimethylindolizidines (LXXXIV)–(LXXXVII) leads to salts whose configurations are claimed[14] to consist of the fixed preferred conformation of the bases, compound (LXXXVI) giving rise to a mixture of the *cis*- and *trans*-fused forms[14].

The ^{1}H NMR spectrum of protonated pyrrolizidine agrees with the hypothesis of a *cis*-junction between the rings in the cation of compound (CXXIX).[126] Protonation of the nitrogen atom in heliotridene leads to an increase, relative to the free base, of the fraction of the conformation with an *endo*-puckered saturated ring; (CXXXA):(CXXXB) = 1 : 3.[97]


(CXXIX) (CXXXA) (CXXXB)

The structures of the quinolizidine alkaloids neothiobinupharidine,[168,169] thiobinupharidine[170] (hydrated dihydrobromides), poranthericine,[171] porantherine,[172] and vertaline[173] (hydrobromides) were elucidated by X-ray diffraction. It has been shown that the quinolizidine rings in capaurine hydrobromide[138] and isocapaurimine hydrobromine monohydrate[174] have a *cis*-junction between the rings[138,174].

Analogous studies have been made on compounds of the pyrrolizidine series. The absolute configuration was found and the bond lengths and valence angles were determined in the hydrobromide of *cis*-1,8-*E*-1-carboxypyrrolizidine (CXXXI).[175] Application of the method of anomalous dispersion made it possible to establish the absolute configuration of the dihydrochloride (CXXXII).[176]


(CXXXI) (CXXXII)

The structure of nitropolyzonamine, in the form of its perchlorate, has been elucidated. The pyrrolizidine rings in this compound have the envelope conformation (C_s).[177]

It has been shown[178] that the 1,2-dehydropyrrolizidine skeleton in jacobine hydrobromide exhibits has an *exo*-puckered and twisted saturated ring.

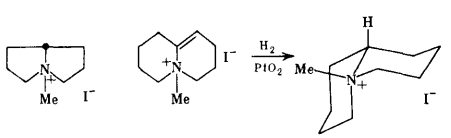
The conversion of the tertiary nitrogen in quinolizidines, indolizidines, and pyrrolizidines into a quaternary form leads to the fixation of the *cis*- or *trans*-junction between the rings[9]. A convenient criterion for the determination of the configurations of *N*-methylquinolizidinium and *N*-methylindolizidinium ions is the chemical shift of the protons in the methyl group attached to the nitrogen [9,12,179]. The reliability of this criterion demonstrated the agreement between NMR and X-ray diffraction data[180-182]. However, this method is applicable only to methiodides without a substituent in the angular position. If different substituents (except CN) are located in the 10-position in quinolizidinium salts, the signal of the $\geq^{+}$N–Me group in the *cis*-fused salts occurs at a higher field than for the *trans*-fused compound[183]. At the same time the configurational assignment of quaternary quinolizidinium salts can be achieved on the basis of the measurements of the half-widths of the signals of the $\geq^{+}$N–Me group. Thus *trans*-fused *N*-methylquinolizidinium has a half-width of the methyl singlet of 1.53 Hz, while the *cis*-fused salt has a corresponding width of 0.96 Hz.[184] It has been suggested that this criterion is applicable to other *N*-methylated heterocycles of a similar type[184].

The stereochemistry of quinolizidine methiodides with a single substituent in the 10-position can be readily inferred from the number of signals in their ^{13}C NMR spectra—the *trans*-fused salts have a plane of symmetry which gives rise to four signals due to the ring nuclei.[183]

One must note that the type of junction between the rings in the quaternary salt and in the free base may be the same[69,70], but in the general case this is not necessarily so[179]. Instances are known where the base has a preferentially *trans*-fused conformation, but gives rise either to a *cis*-fused salt [166,185,186] or to a mixture of epimers[12,64,186].

With the exception of the case of intramolecular quaternisation, which is possible only for a *trans*-junction between the rings[125], it is believed that pyrrolizidines usually form unstrained *cis*-fused salts[7]. On reaction with methyl iodide, pyrrolizidine gives a single *cis*-fused quaternary salt (**CXXXIII**), which has been confirmed by its ^{1}H NMR spectrum[126].

The *cis*-junction between the rings in the quaternary salt (**CXXXV**) is regarded as a consequence of the catalytic hydrogenation of the unsaturated compound (**CXXXIV**) from the sterically least hindered side of the molecule[81,187].



(CXXXIII) (CXXXIV) (CXXXV)

By comparing the optical rotations of (+)-epilupinine and (–)-lupinine and the methiodides obtained from the bases, it has been shown that the quaternary salts have respectively *trans*- and *cis*-junctions between the rings. The configurations (*cis*- and *trans*-) of the methiodides prepared from optically active 1-methylquinolizidines have been demonstrated similarly[81].

Crystalline quaternary salts have been investigated by X-ray diffraction. In the quinolizidine series an example of this type of investigation is provided by the determination of the nature of the junction between the rings in α- and β-methiodides of hunterburnine.[180,181] The study of the steric structures of the methiodides of alkaloids with an indolizidine fragment–kopsanone [189] and tylophorinidine [190]—yielded data for the absolute configurations of these alkaloids. In the pyrrolizidine-based thelepogine methiodide *exo*-puckering of the saturated five-membered ring is observed (angle of deflection 55°),[191] while in the cation of the diester of 8-hydroxymethylretronecine the unsaturated ring exhibits *endo*-puckering and is somewhat twisted[192].

The arsenal of available physical and physicochemical methods makes it possible to determine the configurations and preferred conformations of both the simplest bases and complex natural products of the quinolizidine, indolizidine, and pyrrolizidine series. In many of the studies quoted, a combined application of various methods was achieved in the course of stereochemical investigations, which yields the most reliable results.

A quantitative description of the conformational equilibria of 1-azabicyclic systems in liquid and gaseous phases has remained difficult hitherto. In the immediate future the situation is most likely to change in connection with the introduction of the interesting method of the kinetically controlled protonation of amines,[193] which has been studied in detail and which makes it possible to detect invertomers in the form of the corresponding cations. The ratio of the latter is determined by NMR.[193]

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Preparation and Reactions of Chloro-derivatives of Nitriles

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Published information on the synthesis and reactivity of chloro-derivatives of nitriles is summarised, and methods are examined for the preparation of such derivatives of acetonitrile, acrylonitrile, methacrylonitrile, crotononitrile, and benzonitrile. Research on the mechanism of reactions undergone by the derivatives is reported. A list of 113 references is included.

CONTENTS

I. Introduction 282
II. Preparation of chloro-derivatives of nitriles 282
III. Reactions and practical application 285

I. INTRODUCTION

The use of nitriles, in particular acrylonitrile, in aeronautics, motorcar manufacture, building, light industry, and agriculture, as well as exploitation of the high calorific value of several nitriles in special fuels, explains the continuously increasing production of several nitriles.

The presence of a chlorine atom in nitriles increases the synthetic and practical possibilities of this class of compounds. Chloro-derivatives of nitriles are of both theoretical and practical interest, and have therefore attracted the attention of research workers. Such compounds are intermediates in various organic synthesis, while unsaturated chlorinated nitriles find application in the production of polymers having interesting properties.

The little information available on the synthesis of chlorinated nitriles has appeared mainly in the patent literature. Only two books have been published on fundamental aspects of the reactivity of nitriles[1,2]. No systematic results are available on the preparation and reactivity of the halogeno-derivatives. Since 1960 papers have appeared on the synthesis of chloro-derivatives of nitriles, and during the past 5-7 years several investigations of the reactivity of chloroacrylonitriles have been published. The present Review summarises results for the preparation of chloro-derivatives of nitriles and investigations of their reactions.

II. PREPARATION OF CHLORO-DERIVATIVES OF NITRILES

Direct chlorination is one of the main methods for obtaining chloro-derivatives of nitriles. The earliest papers on this process appeared during the nineteenth century[3-5]. Acetonitrile is readily chlorinated to give a high yield of trichloroacetonitrile:

$$CH_3CN + 3Cl_2 \rightarrow Cl_3CCN + 3HCl\ .$$

Chlorination can be initiated photochemically with natural or artificial radiation (at 50-80°C), catalysed by platinum or silver chloride on asbestos, or effected by a combination of these treatments[6,7,9]. The reaction is also accelerated by preliminary saturation of the acetonitrile with hydrogen chloride.

Publications on liquid-phase chlorination reflect no generally accepted view on why interruption of the process does not prevent the formation of completely chlorinated products. Analysis of the reaction mixture shows the absence of mono- and di-chlorinated derivatives of acetonitrile. Stepanov and Shirokova[8] explain such discrepancies on the assumption that the rate of chlorination of the starting material is considerably lower than those of the partly chlorinated products. In the Reviewer's opinion such a hypothesis is implausible as it is devoid of analgies. Carboxylic acids and their derivatives can readily be chlorinated in stages, which applies also to many other compounds containing activated methyl and methylene groups. A more plausible hypothesis is that hydrogen chloride liberated on chlorination adds to the partly chlorinated nitrile, and the resulting nitrilium salt or tautomeric imidoyl chloride is chlorinated considerably more rapidly than is the initial nitrile:

$$CH_3CN + Cl_2 \xrightarrow{\text{slow}} (ClCH_2{-}C{\equiv}NH)^+Cl^-$$
$$(CH_2Cl{-}C{\equiv}NH)^+Cl^- + Cl_2 \xrightarrow{\text{rapid}} (CHCl_2{-}CNH)^+Cl^- + HCl$$
$$(CHCl_2{-}CNH)^+Cl^- + Cl_2 \xrightarrow{\text{rapid}} (CCl_3{-}CNH)^+Cl + HCl$$
$$(CCl_3{-}CNH)^+Cl^- \rightarrow CCl_3{-}CN + HCl.$$

On this hypothesis it was deduced[9] that preliminary treatment of the nitrile with hydrogen chloride should increase its rate of chlorination, which was fully confirmed by experiment.

A process suggested[10] for the continuous catalytic production of chloroacetonitrile CH_2ClCN consists in the gaseous chlorination of acetonitrile. The latter is treated with chlorine diluted with an inert gas at temperatures from 50°C to the boiling point of acetonitrile, with simultaneous exposure of the mixture to light from a mercury lamp or ionising rays[11]. Acetonitrile vapour and chlorine can also be passed through a turbulent-flow reaction vessel[12].

Several publications have appeared on the preparation of chloro-derivatives of acrylonitrile. Methods are based either on direct chlorination or on the dehydrochlorination of $\alpha\beta$-dichloropropionitrile[13,14]. Table 1 lists conditions for the chlorination of acrylonitrile[15-32]. The action of a hydrohalic acid on propiolonitrile in the presence of a copper salt has been claimed[18] to give a 75% yield of a β-halogeno-derivative of acrylonitrile. Processes have been reported for obtaining α-halogenoacrylonitriles[19] by the dehalogenation of $\alpha\alpha\beta$-trihalogenopropionitriles by treatment with a trialkyl or a triaryl phosphite:

$$XCH_2CX_2CN + (RO)_3P \rightarrow CH_2{=}CXCN + (RO_2)POX + RX$$
$$(X{=}Cl, Br, I)\ .$$

A 91% yield of $\alpha\alpha\beta$-trichloropropionitrile has been claimed[21] when a hydrogen halide is introduced into the chlorination of acrylonitrile. The action of chlorine on

propiolonitrile in an alcoholic or aqueous-alchoholic solution of a copper(II) halide at 30–60°C is stated[22] to give di- and tri-halogenated derivatives of acrylonitrile. Another method has been suggested[23] for obtaining $\alpha\alpha\beta$-trichloropropionitrile, which is very effective in suppressing the growth of weeds among broad-leaved plant crops (Table 1).

Table 1. Conditions of chlorination of acrylonitrile (ACN).

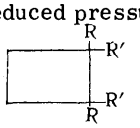
Starting materials	Temp., °C	Catalyst	Contact for	Yield, wt.%			Ref.
				α-ClACN	β-ClACN cis + trans	α,α,β-trichloropropionitrile	
ACN + Cl_2	200—550	activated carbon	—	68	—	—	15
ACN + Cl_2 (1-3:1)	450—850	—	0.001-1 s	90	—	—	16
ACN + Cl_2	100—600	chlorides or oxides of Cu, Cr, Ni, Mn, Mg, Al, Fe, Ca, Pd, V	—	90	—	—	17
α-Acetoxy-β-chloropropionitrile (pyrolysis)	535	—	—	28	35	35	26
ACN + Cl_2	50—70	CCl_4, $CHCl_3$ soln.	—	—	—	95	23
αβ-Dichloropropionitrile (pyrolysis)	60 (12 mm)		0.7 s	93	—	—	29
αα-Dichloropropionitrile + NH_3	0—15	—	0.5-1 h	64	—	—	31
ACN + O_2 + HCl	150—160 (0.1-10 atm)	—	1-30 s	32.6	—	—	32

A paper on the synthesis and polymerisation of several α-substituted acrylonitriles has reported[25] preparations of α-bromoacrylonitrile, α-chloroacrylonitrile, methylenemalononitrile, methacrylonitrile, and other alkylated acrylonitriles. Isomeric mixtures of *cis*- and *trans*-β- and -α-chloroacrylonitriles can be obtained[26] by the pyrolysis of α-acetoxy-β-chloropropionitrile. Chlorination of acrylonitrile in dimethylformamide will give an approximately 90% yield of αβ-dichloropropionitrile[27]:

$$CH_2{=}CH{-}CN + Cl_2 \xrightarrow{DMF} CH_2Cl{-}CHCl{-}CN .$$

An interesting study[28] of the influence of gaseous hydrogen chloride on the chlorination of acrylonitrile showed that, depending on the concentration of the gas evolved, either a mixture of β-mono- and ααβ-tri-chloropropionitriles or αβ-dichloropropionitrile is formed. If chlorination is continued after the solution has become saturated with hydogen chloride, the mixture is formed; continued chlorination of this mixture yields only ααβ-trichloropropionitrile. If the reaction is terminated before the solution begins to be saturated with hydrogen chloride, the main product is αβ-dichloropropionitrile.

Nitriles of α-halogenoacrylic compounds can be obtained by the pyrolysis under reduced pressure of compounds of general formula



where R = Cl and R′ = CN.[29] Clorination of acrylonitrile with a mixture of carbon monoxide and chlorine yields αβ-dichloropropionitrile[30]:

$$CH_2{=}CH{-}CN \xrightarrow{CO+Cl_2} CH_2Cl{-}CHCl{-}CN ,$$

The patent literature[31,32] gives several methods for obtaining α-chloroacrylonitrile (Table 1).

The first publications on the preparation of chloro-derivatives of methacrylonitrile appeared around 1950.[34,35] A proposed method was to chlorinate αβ-unsaturated nitriles at high temperatures (up to 600°C). A mixture of βω-dichloromethacrylonitrile with a 61% yield of ω-chloromethacrylonitrile was obtained:

$$CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2Cl}{\overset{|}{\underset{|}{C}}}}{-}CN + Cl_2 \xrightarrow{585-600^\circ C} \underset{8\%}{CHCl{=}\overset{\displaystyle CH_2Cl}{\overset{|}{C}}{-}CN} + \underset{61\%}{CH_2{=}\overset{\displaystyle CH_2Cl}{\overset{|}{C}}{-}CN} + HCl .$$

Kondratenko and Khaskin[36] have obtained isomeric chlorohydroxyisobutyronitriles by reaction between methacrylonitrile and chlorine in an aqueous medium. Nitriles of 2-chlorocyclobutanecarboxylic acids have been claimed[37] as products of the cycloaddition of vinyl chloride to acrylonitrile. ω-Chloromethacrylonitrile can be obtained[38] by the action of anhydrous liquid ammonia on αβ-dichloro-α-methylpropionitrile. Lower (C_{3-7}) ω-chloro-nitriles result[39] from the telomerisation of cyanogen chloride and ethylene in the presence of azoisobutyronitrile or di-t-butyl peroxide under 52.5–70 atm.

The few publications that have appeared on halogeno-derivatives of the isomeric crotononitrile relate mainly to the formation of γ-chlorobutyronitrile, αβ-dichlorobutyronitrile, and a small quantity of α-chlorocrotononitrile. Table 2 gives several methods for obtaining chloro-derivatives of crotononitrile under various conditions[40–46].

Table 2. Conditions of treatment of crotonitrile with chlorine.

Temp., °C	Catalyst	Yield of chloro-derivative, wt.%		Ref.
		β-mono	αβ-di	
20—250	—	55—61	—	40—42, 44
595—700	—	57,7	—	43
400—600	—	62	—	45
680	metal oxides	—	91	46

Halogeno-derivatives of aromatic nitriles are used for the synthesis of dyes distinguished by excellent fastness, as well as herbicides, insecticides, etc. The very few publications on the preparation of halogenobenzonitriles relate mainly to the *o*-chloro-derivative, which is the principal starting material for the production of azo-dyes, e.g. Basic Bordeaux, Disperse Violet, etc. Several methods are known for obtaining halogenobenzonitriles by the oxidative ammonolysis of halogenated aromatic hydrocarbons. Application of this process to *p*-chlorotoluene on a catalyst comprising arsenic and vanadium oxides promoted with alkali metals at 250–300°C gives a 66.5% yield of *p*-chlorobenzonitrile[47]. A catalyst comprising vanadium(V) and

iron(III) oxides on alumina can also be used[48]. Table 3 lists conditions for the oxidative ammonolysis of chlorotoluene[49–52].

Table 3. Conditions of formation of chlorobenzonitriles*.

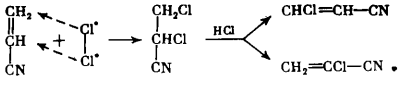
Starting materials	Temp., °C	Catalyst	Yields of isomers, wt.%			Ref.
			ortho	*meta*	*para*	
o-, *m*-, *p*-$ClC_6H_4CH_3$ + O_2 + NH_3 + H_2O*	455	V, Ti, Sn oxides	—	50–80	47	49
p-ClC_6H_4CN + Cl_2	350	V, Sb, Bi, Al oxides	18	49.5	32.5	51
p-ClC_6H_4CN + Cl_2	450	V, Sb, Bi, Al oxides	25	45	30	52

* Proportions of starting materials $ClC_6H_4CH_3 : O_2 : NH_3 : H_2O = 1 : 83 : 19 : 105$.

However, the technical complexity of the suggested methods and the need for expensive catalysts led to the proposal that interesting monomers should be obtained by a single-stage method[53–55] of chlorination of nitriles. A technical scheme has been put forward[57] for the chlorination of C_{2-4} nitriles, in which the reaction vessel contains a stationary layer of catalyst. Since the type of catalyst (perlite, quartz, AG-3 activated carbon) had no clear effect on the yield of products[56], and perlite is inexpensive and readily available, subsequent investigations were made on this catalyst. The highest yields of chloro-nitriles have been observed[57–61] with a molecular ratio of nitrile to chlorine of 2 : 1. With a short period of contact, however, dichloro-derivatives are formed: i.e. chlorine is added. As the time of contact lengthens, α- and β-chloro-nitriles are formed; the maximum yield (80–85 wt.%) is achieved with a time of contact of 5–6 s. Chlorination thus follows an anomalous course, as a consequence of dehydrochlorination of $\alpha\beta$-dichloropropionitrile: i.e. substitutive chlorination takes place. The influence of temperature on the yield of chloro-nitriles is similar to that of the time of contact: at low temperatures dichloro-derivatives are formed, but with rise in temperature their yield diminishes, and that of monochloro-nitriles increases in proportion. Experiments and calculations[62,64] have made it possible to establish optimum conditions for obtaining chloroacetonitrile, α-chloroacrylonitrile, and ω-chloromethacrylonitrile.

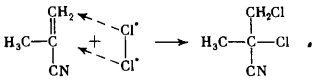
The kinetic and other studies of the chlorination of acrylonitrile and methacrylonitrile have led to a tentative reaction mechanism[57,63,64] in which these nitriles are regarded to a first approximation as unsaturated hydrocarbons[65]. The unusual course of chlorination of the latter was first observed during the nineteenth century[66–69]. Tishchenko[70–74] later found that anomalous chlorination of unsaturated hydrocarbons is observed when a quaternary carbon atom is adjacent to the double bond; the main product is then an isomeric monochloride in which the double bond has been displaced, accompanied by only a small quantity of the dichloride.

On the basis of the mechanism of the anomalous chlorination of hydrocarbons it has been suggested[57–64] that the chlorination of acrylonitrile can be represented by the scheme

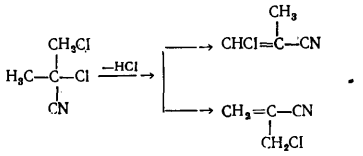


Chlorine adds to the acrylonitrile molecule, the double bond opens, and $\alpha\beta$-dichloropropionitrile is formed. At high temperatures this is accompanied by dehydrochlorination of the dichloro-derivative to give α- and β-chloroacrylonitriles. This scheme is supported by experiment, since at sufficiently high temperatures (350–380°C) with contact lasting for 6–7 s the competitive addition of both chlorine atoms to acrylonitrile diminishes, and a monochloro-nitrile is formed.

The chlorination of methacrylonitrile can probably be represented

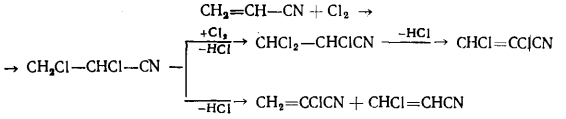


However, the product is unstable, and stabilisation occurs by elimination of hydrogen chloride to form ω-chloromethacrylonitrile:

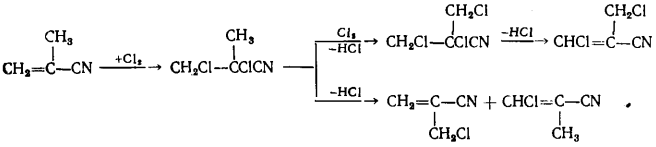


The direction of the dynamic effect is opposite to that of the static effect of conjugation. Therefore methacrylonitrile undergoes chlorination under more severe conditions than does acrylonitrile.

On the basis of the above investigations and the classical interpretation of the anomalous chlorination of unsaturated hydrocarbons it has been suggested[57,64] that the chlorination of acrylonitrile can be represented by the scheme

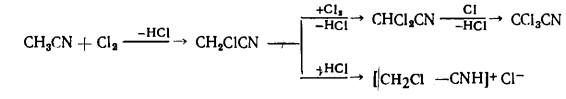


and that of methacrylonitrile by



Adequate attention has been paid to aspects of the liquid-phase chlorination of acetonitrile[33,75,76]. Chlorination involves intermediate formation of a nitrilium salt to give finally trichloroacetonitrile.

The vapour-phase chlorination of acetonitrile with a molecular ratio nitrile : chlorine = 2 : 1 at 350°C for 5–6 s gives mainly chloroacetonitrile with a small quantity of trichloroacetonitrile[57,58,100]. Two fractions corresponding to these products were isolated. Hardly any dichloroacetonitrile was observed. Traces of a nitrilium salt are also formed[100]. The salt decomposes at high temperatures, so that it cannot be formed in vapour-phase chlorination at 350–360°C. The nitrilium salt is most probably formed on cooling, when chloroacetonitrile reacts with hydrogen chloride. From the above considerations the mechanism



has been suggested for the chlorination of acetonitrile.

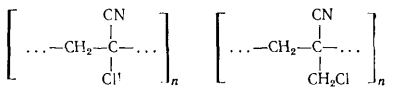
It has thus been ascertained that the vapour-phase chlorination of nitriles follows the anomalous chlorination mechanism of unsaturated hydrocarbons. This method can be used also to obtain unsaturated monochloro-derivatives of other classes of compounds.

III. REACTIONS AND PRACTICAL APPLICATION

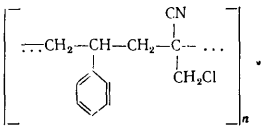
Chloro-derivatives of nitriles find application as insecticides. They also exhibit bactericidal properties[24], and are very effective against soil pests[109].

Chloro-derivatives of nitriles are a little investigated class of compounds. Few papers have appeared on the reactions of the unsaturated representatives, since hitherto they have been unavailable. Development of methods for the preparation of chloro-derivatives of aliphatic and aromatic nitriles has made it possible to study their reactions. A process has been claimed[20] for obtaining derivatives of α-chloro-β-p-hydroxyphenylpropionitrile, which can be used as intermediates in the production of medicinals.

Polymeric materials obtained from chlorine-containing monomers possess valuable properties, in particular fire resistance. The presence of a nitrile group together with a chlorine atom in a monomer may confer on the polymers also frost resistance, gas impermeability, and resistance to corrosive media. It is therefore of practical interest to study the polymerisation of chloroacrylonitrile and chloromethacrylonitrile as examples of such monomers. α-Chloroacrylonitrile has been used[77-81] to obtain polyconjugated polymers both of linear (polyvinylene) structure and of ladder structure with fused naphthyridine rings. As well as the synthesis of homopolymers



the possibility has been investigated of the copolymerisation of chloromethacrylonitrile with styrene to give



Chloroacrylamides have been obtained[82] by conversion of the nitriles into amides under conditions of acid hydration:

$$CH_2{=}CCl{-}CN \xrightarrow{HOH} CH_2{=}CCl{-}C(=O)NH_2 .$$

Chloro-derivatives of nitriles are interesting starting materials for the single-stage preparation of chloro-derivatives of unsaturated acids by hydration in the presence of 75% sulphuric acid. Such acids can be formed also[82-85,105] by direct chlorination of acrylic and methacrylic acids:

$$CH_2{=}CCl{-}CN \xrightarrow{HOH} CH_2{=}CCl{-}COOH \xleftarrow[150-170^\circ]{Cl_2} CH_2{=}CH{-}COOH .$$

Addition of alcohols to α-chloroacrylonitrile in the presence of AV-17 anion-exchange resin, sodium methoxide, and amines is catalysed by the amines themselves[86-89]:

$$ROH + CH_2{=}CCl{-}CN \rightarrow ROCH_2CHCl{-}CN$$

R=CH_3, $CH_2{-}CH{=}CH_2$, $CH_2C{\equiv}CH$

$$R_2NH + CH_2{=}CCl{-}CN \rightarrow R_2NCH_2CHCl{-}CN$$

R′=R=C_3H_7; R=R′=CH_3; R=R′=C_2H_5; R=R′=C_4H_9 .

Nucleophilic substitution by treatment with alcohols has been used to examine the reactivity of the chlorine in chloro-nitriles and to develop a procedure for obtaining hydroxy-derivatives of aliphatic nitriles[90,91]. The reactions of C_1–$_7$ aliphatic alcohols and of cyclic and unsaturated alcohols have been studied[110]:

$$ClCH_2CN + ROH \xrightarrow{NaOH} NCCH_2OR + NaCl + HOH$$

R=CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15},



, $CH_2{-}CH{=}CH_2$, $CH_2{-}C{\equiv}CH$,

$C(CH_3)_2{-}C{\equiv}CH$.

Organosilicon nitriles are obtained by condensing incompletely substituted silanes with alkenes[107,108]. Unsaturated nitriles react with silicochloroform and with alkylchlorosilanes:

$$CH_2{=}CH(CH_2)_n CN + CH_3SiCl_2H \xrightarrow{n\geqslant 1} (CH_3)Cl_2SiCH_2CH_2(CH_2)_n CN .$$

Petrov et al.[92] studied the addition of alkoxysilanes to but-3-enonitrile, β-allyloxypropionitrile, and acrylonitrile, and established that addition conforms to the equation

$$R'(RO)_2SiH + CH_2{=}CHCH_2X \rightarrow R'(RO)_2SiC_3H_4CH_2X$$

R′=CH_3, OC_2H_5, OCH_3; R=CH_3, C_2H_5; X=OCH_2CH_2CN, —CN.

Condensation of acrylonitrile, 2-vinylpyridine, and methacrylaldehyde with triethoxysilane and several other partly substituted silanes in the presence of activated AV-16 anion-exchange resin yields β-triethoxysilylpropionitrile and other silicon-containing nitriles[94-99].

Golubtsov et al.[93] investigated the reactions of methyldichlorosilane with acrylonitrile in the presence of various catalysts (pyridine, chloroplatinic acid), but did not achieve satisfactory results.

The action of a silicon–copper catalyst on β-chloropropionitriles forms β-trichlorosilylpropionitrile[101]:

$$ClCH_2CH_2CN \xrightarrow{Si/Cu} \begin{cases} \rightarrow HSiCl + SiCl_4 \\ \rightarrow CH_2{=}CH{-}CN \\ \rightarrow Cl_3SiCH_2CH_2CN \end{cases} .$$

Mono-, di-, and tri-nitriles containing chlorine attached to silicon have been obtained[102,103] directly from chloroacetonitrile, α-chloroacrylonitrile, and ω-chloromethacrylonitrile:

$$RCl \xrightarrow{Si/Cu} \begin{cases} \rightarrow HSiCl_3 + SiCl_4 \\ \rightarrow R_nSiCl_{4-n} \end{cases}$$

R=CH_2CN, $CH_2{=}C(CN){-}$, $CH_2{-}C(CN){=}CH_2$; $n = 1$–3 .

These workers[103,104] examined the reactions of chlorosilylated nitriles, and have established[111] that silicon-containing nitriles can be obtained by condensation of a silanol with a chlorinated nitrile:

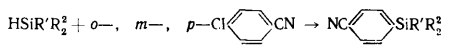
$$R_3SiOH + ClR'CN \rightarrow R_3SiOR'CN$$

R=CH_3; R′=$-CH_2-$, $-C(=CH_2)-$, $-CH_2-C(=CH_2)-CH_2-$, $-CH{=}CH-$, $-CH{=}C(CH_3)-CH_2-$, $CH_3-CH{=}C(\ )-$.

The products can be converted by hydration into unsaturated organosilicon acids:

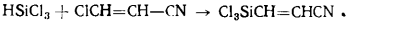
$$R_3SiOR'CN \xrightarrow[H_2SO_4]{HOH} R_3SiOR'COOH .$$

An original synthesis of organosilicon nitriles was suggested by Chernyshev and his coworkers[112,113]. *o*-, *m*-, and *p*-Trichlorosilylbenzonitriles and the corresponding methyldichlorosilyl compounds have been obtained[112] from a hydrolytic mixture of trichlorosilane or methyldichlorosilane with the appropriate chlorobenzonitrile in the gas phase at 500–650° C for a very short period of contact (10–90 s), after which the products were separated:

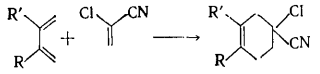


$R'=R^2=Cl$; $R'=CH_3$, $R^2=Cl$.

The same workers suggested[113] gas-phase pyrolysis of silicochloroform or methyldichlorosilane with β-chloroacrylonitrile or αβ-dichloroacrylonitrile at 500–650° C for 10–100 s to obtain the chlorosilylacrylonitriles:

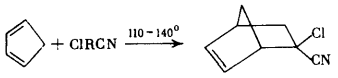


Like acrylonitrile chloro-derivatives of nitriles condense with dienes. The diene condensation of α-chloroacrylonitrile with butadiene, isoprene, etc. can be represented[87]



R=R′=H; R=H, R′=CH_3; R=H, R′=Cl; R=Cl, R′=CH_3; R=R′=Cl.

Bicyclic chloro-nitriles have been synthesised[106] by the diene condensation of α-chloroacrylonitrile and ω-chloromethacrylonitrile with cyclopentadiene:



The above survey shows that development of the preparation of chloro-derivatives of nitriles offers great promise, since the resulting monomers possess wide synthetic possibilities and have important applications.

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Advances in the Chemistry of 1,2-Azoles

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Data obtained during 1960-1977 on the physical, physicochemical, and chemical properties of 1,2-azoles are surveyed. For the first time such data are subjected to comparative discussion to reveal common features and differences in properties. A list of 304 references is included.

CONTENTS

I. Introduction 289
II. Electronic structure with physical and physicochemical properties 289
III. Reactions with retention of heterocyclic ring 292
IV. Reactions with cleavage of heterocyclic ring 297

I. INTRODUCTION

1,2-Azoles include pyrazole, isoxazole, and isothiazole. Their derivatives have long found practical application: it is sufficient to mention the medicinal products—antipyretics of the pyrazolone series[1], sulphanilamides, and semi-synthetic penicillins containing the isoxazole ring[2]. During recent years isoxazole derivatives have come to be widely used in organic synthesis to obtain various heterocycles, peptides, steroids, and other naturally occurring compounds[3,4].

The chemistry of each of the 1,2-azoles has been considered in detail in a series of reviews published during the past 15 years—three on pyrazoles[1,5,6], five on isoxazoles[2-4,7,8], and two on the "youngest" class, the isothiazoles[9,10]—but they contain no comparative analysis of the properties of 1,2-azoles. Such comparison has been made in the books by Katritzky and Lagowski[11] and by Paquette[12], although the very condensed treatment results in a fragmentary description, which is accompanied also by inaccuracies and simple errors[12].

The nature of the heteroatom distinguishing one 1,2-azole from another not only determines the character of the bond between this atom and the nitrogen atom, of course, but also influences the properties of the molecule as a whole. The present Review has been written with the aim of revealing common and distinguishing features in the physical and chemical properties of heteroaromatic 1,2-azoles: it contains neither methods of preparation of azoles nor the properties of their hydrogenated derivatives. Considerable difficulties in compiling the Review arose from the need for selection from the ~800 publications on the properties of 1,2-azoles that have by now appeared (Autumn 1977). In order to avoid greatly increasing the length of the Review, references are given to existing reviews and attention is directed to information from publications not mentioned in them, as well as the most important fundamental work that has appeared since 1960.

II. ELECTRONIC STRUCTURE WITH PHYSICAL AND PHYSICOCHEMICAL PROPERTIES

1. Quantum-chemical Calculations and Molecular Geometry

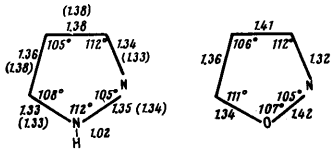
The simple LCAO-MO method has been used in the Hückel approximation to calculate molecular diagrams for pyrazole[13,14], isoxazole[15,16], and isothiazole[17]. The calculations showed that all the 1,2-azoles possess 6π-electron shells, and are therefore heteroaromatic systems. Since different values were used by different workers for the Coulombic and resonance integrals, only qualitative comparison of their molecular diagrams is possible. In all the 1,2-azoles the excess π-electron density is concentrated on the "pyridine" nitrogen and the $C_{(4)}$ atoms, while the second heteroatom bears a positive charge. The π-electron charges on the $C_{(3)}$ and $C_{(5)}$ atoms are either positive or negative depending on the heterocycle and on the parameters α and β. The highest bond orders have been found for the $C_{(3)}-N$ and $C_{(4)}-C_{(5)}$ bonds, and the lowest order for the bond between the heteroatoms. Calculations have also been made by the Pariser–Parr–Pople (PPP)[18,19] and other semi-empirical methods[20]. Especially noteworthy are the calculations which Witanowski et al.[18] made on all three 1,2-azoles by the same method.

More accurate results have been obtained by taking the σ electrons into account[21]. During the 1970s improved methods of calculation, including CNDO/2 have been used to elucidate the electronic structures of pyrazole and isoxazole[22], alkylpyrazoles[23], and phenylisothiazoles[24].

Many experimental characteristics of 1,2-azoles correlate well with quantities calculated by quantum-chemical methods. Thus the LCAO-MO method has yielded values agreeing with experiment for dipole moments[16,25], $\pi \rightarrow \pi^*$ transition frequencies in absorption spectra[14,19], and quadrupole interaction constants in the gas phase[25]. The PPP method gives good results for calculating the first ionisation potential[19] and the π-electron density on the nitrogen atoms[18]; and the CNDO/2 method for determining the total electron density on the "pyridine" nitrogen atom[23] and the carbon atoms[22,26], as follows from determinations of basicity and the hydrogen-1 and carbon-13 chemical shifts. Thus, as for other systems, no single method of quantum chemistry can be recommended for predicting all experimental results.

The literature contains much information on bond lengths and angles in the pyrazole ring, less on the parameters of the isoxazole ring, and hardly any on those of the isothiazole ring[280]. Such data have usually been obtained by X-ray diffraction[27,28] (see diagram); the parentheses in the diagram enclose bond lengths determined for pyrazole by neutron diffraction[29]. A striking feature of the parameters given in the diagram for the pyrazole ring in the crystalline state is the equalisation of carbon–nitrogen and carbon–carbon bond lengths, which indicates smoothing of the difference between "pyridine" and "pyrrole" nitrogen atoms and a high degree

of delocalisation of π bonds. Nevertheless, it has been firmly established that the hydrogen atom forming the nitrogen–hydrogen bond is attached solely to $N_{(1)}$.[29] The nitrogen–carbon bond lengths are close to the length 1.35 Å of the corresponding bond in pyridine; the carbon–carbon bonds in pyrazole are shorter than those in benzene (1.395 Å); and the nitrogen–nitrogen bond is shorter than the sum of the covalent radii of the nitrogen atoms (1.40 Å). All these data are evidence of the stability of the pyrazole molecule, which is confirmed by the chemical reactions of the heterocycle. For the variation in the bond lengths of the ring in the vapour state see Ref. 30.



Bond lengths (in Å) and angles in 1,2-azoles.

Since unsubstituted isoxazole is a liquid, X-ray diffraction has been applied to its crystalline derivatives[28,31], the results of which have given the mean bond lengths and angles indicated in the diagram for the ring. The nitrogen–oxygen bond is noteworthy, for its length (1.42 Å) exceeds considerably the sum (1.36 Å) of the covalent radii. This is clear evidence of the "looseness" and chemical instability of the bond, in good agreement with the chemical behaviour of isoxazole and its derivatives. On the other hand, the $C_{(5)}-O$ bond is shorter than in furan (1.37 Å). The three remaining bonds are similar in their parameters to the corresponding bonds in pyrazole. In contrast to the latter the largest angles in the isoxazole ring (111–112°) are the $N-C_{(3)}-C_{(4)}$ and $C_{(4)}-C_{(5)}-O$ angles. For variation in bond lengths in the rings of arylazoles see Refs. 32 and 33.

2. Basicity and Ionisation Potentials

1,2-Azoles are Hammett bases[34,35], weaker than pyridine. The pK_a values fall in the sequence from pyrazole through isothioazole to isoxazole (respectively +2.5,[36] −0.5,[35] and −3.0[35]), probably as a consequence of increasing polarisation of the bond between the heteroatoms. Isoxazole derivatives are the weakest bases among all 1,2- and 1,3-azoles, with negative pK_a values[35,37–39]. Their basicities have been determined spectrophotometrically: the potentiometric method used previously would give incorrect results.

French chemists have examined the pK_a values for 90 pyrazoles, and found linear relations of the type $pK_a^{calc} = pK_a^0 + \Sigma\Delta pK_m^n$, where pK_a^0 is the value for the pyrazole ring in which the carbon atoms are unsubstituted, while ΔpK_m^n is the effect of a substituent m at position n, which is more correctly characterised by the Hammett σ_{meta} constant[36]. The resulting equations describe the basicity of derivatives of pyrazole and of 1-methyl- and 1-*p*-nitrophenyl-pyrazoles. More complicated correlations have been revealed between basicity and substituent constants in the isoxazole series[37,39].

Pyrazoles in which the nitrogen atoms are unsubstituted are at the same time also weak acids. The acidity of pyrazole itself is extremely slight ($pK_a' \simeq 14$).[40] It is increased by factors of 10^4 when a nitro-group is introduced into the 4 position[41].

The ionisation constants of hydroxy- and amino-derivatives of 1,2-azoles, as well as those of azolecarboxylic acids[42,43], suggest that the azole rings (with the exception of pyrazole at position 4) tend to attract electrons more strongly than does the benzene ring.

The π_3- and n-ionisation potentials of 1,2-azoles and pyridine increase in the sequence[44,45]

pyridine < pyrazole < isothiazole < isoxazole

The N potentials provide an approximate measure of the basicity of these heterocycles, which diminishes in the same sequence.

3. Dipole Moments

A large quantity of data have now accumulated on the dipole moments of pyrazole and isoxazole derivatives: most of the work has been reviewed in Ref. 46. Dipole moments of unsubstituted azoles have been determined from measurements of the dielectric constant in benzene solution[46–48] and from the microwave spectra of the vapours[49–51]; similar results were obtained by the two methods. Special attention must be paid to the necessity of working with dilute solutions of N–H pyrazoles[47,52], owing to the occurrence of association in concentrated solutions. The dipole moments of 1,2-azoles increase on passing from pyrazole to isoxazole, also as a consequence of enhancement of the polarisation of the bond between the nitrogen atom and the other heteroatom. A method proposed recently for calculating dipole moments of azoles gives results that are extremely close to experimental values[53].

Several studies have been made on the influence of substituents on the dipole moments of pyrazole and isoxazole derivatives[48,52,54]. Substituents at position 5 in the ring of isoxazole and 1-methylpyrazole exert a strong influence; a phenyl group has a $+M$ effect in both rings[48,52]. In 1-phenylpyrazole strong $+M$ effects are observed from substituents (amino, chloro, bromo) at positions 3 and 5[54] and from a nitro-group at the *para*-position of the benzene ring[52]. Interesting deductions have been made from the dipole moments (experimental and calculated) of di- and tri-substituted pyrazoles and isoxazoles: a correlation coefficient of 0.982 has been found[48] for 4-substituted 3,5-dimethylisoxazoles between the dipole moment of the group and the Hammett σ_{meta} constants of the substituent. Results for the dipole moments of 4-substituted 3,5-dimethyl(or diphenyl)pyrazoles suggest that structures having a fixed nitrogen–hydrogen bond are present in solution[54].

4. Ultraviolet and Infrared Spectra

The ultraviolet spectra of 1,2-azoles, like those of other five-membered heteroaromatic compounds, contain only absorption bands corresponding to $\pi \rightarrow \pi^*$ transitions[55]. The presence of absorption corresponding to $n \rightarrow \pi^*$ transitions in the spectra of pyrazoles has been a matter of controversy[55,56].

Pyrazole and isoxazole possess similar ultraviolet spectra, but the presence of the sulphur atom in isothiazole leads to absorption at longer wavelengths, as with

other sulphur-containing heterocycles. Most data are available on the spectra of pyrazoles among 1,2-azole derivatives; noteworthy work was done by Grandberg[57] and especially by French chemists, who studied and classified the ultraviolet spectra of 170 pyrazole derivatives[56]. Considerably less work has been done on derivatives of the other 1,2-azoles; mention must be made of a study on the spectra of nitroisoxazoles[58], and also papers on the ultraviolet spectra of substituted isothioazoles[59-61]. The influence of substituents in heterocycles on the position and the intensity of absorption can readily be traced from the ultraviolet spectra. A 4-methyl group causes a bathochromic shift in λ_{max} by 8–9 nm;[56,59,61] the opposite relation—a hypsochromic shift—is observed in the spectra of 3-methylisoxazoles and 5-methylpyrazoles. Such shifts are far larger when acceptor substituents (nitrophenyl groups) are attached to nitrogen in the pyrazoles[56]. Auxochromes (halogen, alkyl, amino) present in a pyrazole ring cause a slight bathochromic shift in λ_{max}; pyrazoles containing chromophoric groups (carbonyl, aryl, nitroso, nitro) absorb at far longer wavelengths (242–282 nm) than occurs in the benzene series[57]. An analogous band in the spectra of alkyl-4-nitroisoxazoles was attributed to conjugation between the nitro-group and the heterocyclic ring[58].

Certain conclusions on conjugation in phenylated azole systems can be drawn from a detailed analysis[16,62] of the ultraviolet spectra of *C*-phenyl derivatives of isoxazole and pyrazole supplemented by spectral data on phenylisothiazoles[59]. In 3- and 4-phenylisoxazoles and in 4- and 5-phenylisothiazoles the benzene ring is conjugated with multiple bonds in the heterocycles. Yet 3-phenylpyrazoles (whether or not *N*-substituted), 3-phenylisothiazole, and 5-phenylisoxazole are single conjugated systems, an effect which is more strongly developed than in biphenyl. Hypsochromic shifts in the spectra of arylpyrazoles observed on passing from mono- to 1,5-di-substituted rings are attributed to diminished conjugation in *C*- and *N*-arylpyrazoles owing to disturbance of coplanarity between the benzene and heterocyclic rings as a consequence of steric interaction between $N_{(1)}$- and $C_{(5)}$-substituents[56,57]. Depolarisation of the Rayleigh scattering indicates[63] that the angle between the planes of the rings in the preferred conformation of 1-phenylpyrazole is 11°; any substituent at position 5 increases the angle and diminishes conjugation. Grandberg et al. studied the fluorescence of 300 pyrazole derivatives[64], and used the spectra to determine the angle between the planes of the rings in 5-substituted 1-phenylpyrazoles[65]. Spectrophotometry has also been employed to investigate steric effects in 4-phenylpyrazoles[66] and 3(5)-arylisoxazole-4-carboxylic acids[67].

The infrared spectra of unsubstituted 1,2-azoles have by now been quite fully studied[68-73]. In the range 1200 to 1600 cm^{-1} three or four characteristic frequencies of each ring are fairly close to frequencies of the other, although simultaneous consideration of the frequencies permits accurate identification of the heterocycle. Absorption in the region of carbon–hydrogen stretching vibrations (3100 cm^{-1}) of variable intensity, which is observed in unsubstituted azoles, may be greatly strengthened in aryl derivatives[74-76].

Systematic investigations have been made also on the infrared spectra of derivatives of isoxazole[42,69,77-79], pyrazole[80], and isothiazole[61,81,82]. From the results general conclusions have been reached on the influence of the number and nature of substituents on the characteristic frequencies of the rings. For example, the raising of the frequency to 1630–1640 cm^{-1} in the spectra of trisubstituted isoxazoles indicates steric interaction between the substituents; in phenylisoxazoles the coplanarity of the rings is disturbed[69].

Raman spectra have been obtained for 1,2-azoles[71-73] and several of their derivatives[73,81,82]. At the present time hardly any use is made of these spectra for solving structural problems or identifying azoles.

5. Nuclear Magnetic and Quadrupole Resonance Spectra

The rapid development of nuclear magnetic resonance spectroscopy during the 1960s led to the appearance of a large number of papers containing results for 1,2-azoles and their derivatives. These related mainly to ^{1}H n.m.r. spectra of pyrazoles[83-85], isoxazoles[86], and isothiazoles[87], but magnetic spectra were also published for resonance on carbon-13[26,88-90] and nitrogen-14[18] nuclei. In the ^{1}H n.m.r. spectra of 1,2-azoles the signals due to 4-protons appear in the highest fields, whereas those due to the two remaining protons of each heterocycle, located in the immediate vicinity of the electronegative heteroatoms, are displaced down field. Certain difficulties arise in assigning signals from the 3- and 5-protons, especially in pyrazole derivatives. The signals of 3-protons in isoxazoles and isothiazoles are broadened owing to incomplete removal of spin–spin interaction between nitrogen and 3-hydrogen atoms as a consequence of quadrupole relaxation of the nitrogen-14 nucleus[91]. The broadening of the 3-hydrogen signal served as a reference in interpreting the 1H n.m.r. spectra of 4-arylisothiazoles, in which the chemical shifts of the 5-protons may be smaller than those of the 3-protons (on the δ scale)[92]. Assignment of the 3- and 5-proton signals in pyrazole derivatives necessitated the preparation of isomers whose structure had been rigorously established, as in the work of Habraken[66,93]. Under the influence of acceptor substituents the signals due to 3- and 5-protons in the ^{1}H n.m.r. spectra of isothiazoles and especially of pyrazoles may change places: the signals due to 5-protons appear down field[84,85,94,95]. Detailed and systematic studies have been made of this inversion[84,95]. The effects of solvents differing in polarity were used to assign the proton signals: dipolar aprotic solvents exert a very strong influence[84,96], and may shift 5-proton signals down field[84].

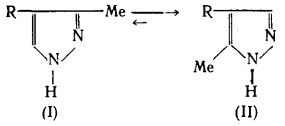
Study of the ^{1}H n.m.r. spectra of arylisoxazoles revealed a linear dependence of the chemical shift of the 4-proton in 3,5-diarylisoxazoles on the Hammett σ_{para} constant at $C_{(5)}$ in the benzene ring[97,98]. Rather earlier a more general relation

$$\delta_4 = \delta_4(s) + \alpha_1 + \alpha_3 + \alpha_5$$

had been discovered in the pyrazole series, in which $\delta_4(s)$ is the chemical shift of the 4-proton of 1,3,5-trimethylpyrazole in a given solvent and δ_4 is the chemical shift of the 4-proton in the substituted pyrazole in the same solvent, while α_1, α_3, and α_5 are the constants of substituents at positions 1, 3, and 5 (they correlate with the Hammett constants)[94].

Spin–spin interaction constants can usually be measured for neighbouring protons in 1,2-azoles[59,85-87]. Their values (1.6–2.3 Hz) are characteristic of all carbon–carbon bonds in azoles other than the $C_{(4)}=C_{(5)}$ bond in isothiazoles ($J_{4,5}$ = 4.5–5.0 Hz). The low values of the constants are probably due to strong polarisation of the bonds of the heteroatoms. The constants $J_{3,5}$ and J_{H,CH_3} are still smaller[99].

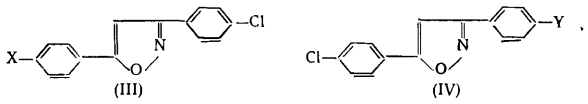
Preferred tautomeric forms and conformations of several substituted pyrazoles in solution have been established from the ^{1}H n.m.r. spectra. Analysing the chemical shifts of ring protons and of methyl groups in *N*-hydro- and *N*-methyl-pyrazoles, Habraken and Moore[93] found that the equilibrium



(I) (II)

is displaced to the right. On the basis of the ^{1}H n.m.r. spectra it is proposed to describe the structure of pyrazolium salts in terms of analogous resonance structures[100].

In contrast to n.m.r. spectroscopy the second type of microwave spectroscopy—nuclear quadrupole resonance—has hitherto been little used for studying derivatives of 1,2-azoles. Only n.q.r. spectra on nitrogen-14 nuclei in pyrazole and *N*-acetylpyrazole have been described; an asymmetry parameter has been found for the "pyrrole" nitrogen atom, which is proportional to the degree of double-bondedness of this atom (~45%).[101] Quadrupole nitrogen-14 nuclear interaction constants have been calculated for pyrazole and isoxazole[102]. Interesting possibilities of the n.q.r. method have been demonstrated by Soviet authors, who find correlations between the chlorine-35 signal frequency and electronic effects of substituents in 3,5-diarylisoxazoles of types



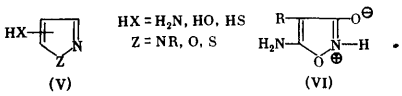
(III) (IV)

which are conjugated systems[103].

6. Tautomerism

This subsection contains a brief account of the tautomerism of hydroxy-, mercapto-, and amino-derivatives of 1,2-azoles, which has been studied by ultraviolet, infrared, and n.m.r. spectroscopy and also by determination of basic or acidic properties. During the past decade Katritzky's reviews and monographs have repeatedly summarised the factual information that has accumulated[11,104,105]. The most recent of these publications[105] gives a clear and concise report on the preferred tautomeric forms of these functional derivatives, but it is based on results that appeared only up to 1968 inclusive, with no references to the work of Soviet scientistis. Below is given a short discussion of the most general data on tautomerism based on work published during 1969–1974.

Azoles containing an amino-group at position 3, 4, or 5, a hydroxy-group at position 3 or 4, or a mercapto-group at position 5 exist as heteroaromatic structures (V)[38,106-110]

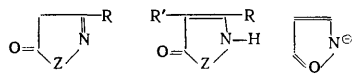


(V) (VI)

Equilibrium formation constants of the zwitterions have been calculated for 4-hydroxyazoles[111]; these are the preferred structures for 5-amino-3-hydroxyisoxazoles (VI).[112]

Complicated tautomerism has been observed in azol-5-ones, especially in *N*-unsubstituted pyrazolones[113].

Quantum-chemical calculations for unsubstituted isoxazol-5-one have shown[114] that the Δ^2(C–H) structure (VII)



(VII) (VIII) (IX)

is advantageous, in agreement with experimental results[115]. 3-Substituted dihydro-5-oxoazoles exist in the same form; in the presence of a 4-substituent these compounds exist in the solid state and in aqueous solution as the Δ^3(N–H) form (VIII), and in non-polar solvents the equilibrium is displaced in favour of the C–H structure[106,116-119]. If the 4-substituent is electron-accepting, the oxo-compounds are strong N–H acids: $pK_a < 2$.[120]

The above results show that 1,2-azoles are heteroaromatic compounds, which are characterised by substitution reactions. However, the presence in every azole of a bond between the heteroatoms that differs from the other bonds leads to variation in the stability of the rings in redox reactions. The nitrogen–oxygen bond in isoxazoles should break the most readily. The peculiarities of the heteroaromatic isoxazole system are probably best explained by Kamiya[19]: stabilisation of the π electrons is caused by electrostatic interaction of two oppositely polarised atoms—nitrogen and oxygen (limiting structure IX)—despite the diminished conjugation in the ring.

III. REACTIONS WITH RETENTION OF HETEROCYCLIC RING

Reactions of this type are in considerable measure characteristic of 1,2-azoles as heteroaromatic compounds. They include substitution in the heterocyclic ring and in a side-chain, and also addition to the ring.

1. Substitution in the Ring

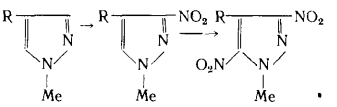
The reactivity indices (localisation energy[14,60], π or total electron density[23,60]) suggest that electrophilic substitution in bases and conjugate acids of pyrazoles and isothiazoles should take place preferentially at carbon atom 4. On the other hand, attack by radicals is directed at positions 5 and 3.[14] For isoxazole the localisation energies indicate preferential substitution at carbon atom 5, independently of the nature of the reactant species; correct conclusions on the direction of attack can be reached on the basis of the calculated π-electron density[15].

(*a*) Electrophilic substitution

Electrophilic substitution is most characteristic of aromatic and heteroaromatic compounds. In the case of nitrogen heterocycles, including 1,2-azoles, the ease of occurrence of such reactions is determined not only by the activity of the reactant species but also by the basicity of the compound and the acidity of the medium. Only in the past decade has study of the reactions of nitrogen-containing heterocycles on the basis of criteria elaborated by Katritzky and Johnson[121] permitted precise establishment of the form (base or conjugate acid) in which the compound reacts. Because of this specific effect it is helpful to discuss separately the electrophilic substitution of 1,2-azoles occurring in strong acids (isotopic exchange of hydrogen, nitration, sulphonation).

Reactions in acid medium (isotopic hydrogen exchange, nitration, sulphonation). In conformity with quantum-chemical calculations and the chemical shifts of nuclei in the n.m.r. spectra, which indicate maximum electron density on the "pyridine" nitrogen atom and carbon atom 4, these are the positions in 1,2-azoles that are attacked by electrophilic species. Attack by a proton on a nitrogen atom gives a protoned base (conjugate acid), whose stability depends on the basicity of the initial azole and the acidity of the medium. Electrophilic substitution at carbon atom 4 then takes place either in the base or in the conjugate acid. Its ease falls in the sequence pyrazole $\gg$ isothiazole $\geqslant$ isoxazole. Thus 4-deuteropyrazole can be obtained by the action of CH_3COOD,[122] but 3,5-dimethylisoxazole undergoes deuterium exchange only under more severe conditions—in a mixture of deuterotrifluoroacetic and dideuterosulphuric acids[123]: both compounds react as the base. On the other hand, the nitration of pyrazole involves the conjugate acid[124]. The first comparative study of the reactivities of 3,5-dimethyl derivatives of *N*-methylpyrazole, isoxazole, and isothiazole towards nitration and isotopic hydrogen exchange in a strongly acid medium was published in 1971.[35] Pyrazole and isothiazole are nitrated as the conjugate acids; deuterium exchange occurs either in the bases or (with an acidity function D_0 exceeding -4.5 to -6.0) in the conjugate acids of these azoles. 3,5-Dimethylisoxazole, the weakest base of the three isosteres, undergoes both reactions as the base. Similar results have been obtained for deuterium exchange in six *N*-methylpyrazoles[125]. French workers[60] have given quantitative data on the reactivities of isothiazole and of its 3- and 5-methyl and 3,5-dimethyl derivatives; their relative rates of nitration are 1 : 2.3 : 4 : 67, i.e. the effect of a substituent is transmitted more strongly from position 5; in 3,5-dimethylisothiazole the effects are non-additive.

Habraken et al.[128–130] and Coburn[131,132] have shown that 1,4-disubstituted pyrazoles (X) can be nitrated at both 3 and 5 positions—compounds (XI) and (XII):

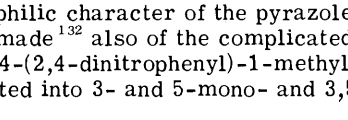


(X) (XI) (XII)

R=Alk, Ar, Br

This unusual orientation on nitration is attributed to the strongly nucleophilic character of the pyrazole ring. A study has been made[132] also of the complicated kinetics of the nitration of 4-(2,4-dinitrophenyl)-1-methylpyrazole, which is converted into 3- and 5-mono- and 3,5-di-nitro-derivatives.

When nitrated in acetic anhydride 5-methyl-1-phenylpyrazole, in contrast to its isomers, gives a mixture of mononitro-derivatives containing 75% of 3-nitropyrazole.[127]. 3(5)-Substituted pyrazoles (XIII) form *N*-nitro-derivatives (XIV), which when heated rearrange into 5-nitropyrazoles (XV):[130]



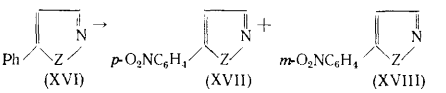
(XIII) (XIV) (XV)

Nitration of 2-hydroxy-1-methylpyrazole yields, as in the case of *N*-hydroxypyridine, a γ-nitro-derivative, i.e. 5-nitropyrazole[133]. The form undergoing the reaction is the base, for which first-order kinetics is observed in the H_0 range from -5 to -6.5; a dinitro-derivative is also formed in a more acid medium.

Unusual orientation—at the 5 position—has been observed also in the sulphonation of 4-methylisothiazole[87]. In the isoxazole series no single example has yet been found of electrophilic substitution at carbon atom 3 or 5 in the ring.

Various physical methods have shown the presence of conjugation in *N*-phenylpyrazole, which favours electrophilic attack at position 4 in the pyrazole base, as follows from nitration in acetic anhydride[1] and the action of chlorosulphuric acid in chloroform[134]. In sulphuric acid the conjugate acid—the *N*-phenylpyrazolium cation—reacts,[127] and the substituent enters the *para*-position of the benzene ring[134], which has only 1% of the activity of unsubstituted benzene[127]. Comparative activities towards nitration have been given[135] for substituted *N*-phenylpyrazoles. In sulphuric acid the nitration of *N*-arylpyrazoles is a first-order reaction; disturbance of the coplanarity of the two rings by $N_{(2)}$- or $C_{(5)}$-substituents in the pyrazole ring diminishes the activity of the benzene ring[127].

Numerous papers have appeared on the nitration and the sulphonation of other mono- and poly-phenylated 1,2-azoles; several later publications have reviewed results obtained earlier[24,92,130,136–141]. Substitution in isomeric 3- and 5-phenyl-azoles occurs in the *para*- and *meta*-positions of the benzene ring, usually with predominant formation of *para*-derivatives:



(XVI) (XVII) (XVIII)

An exception is the preferential appearance of *meta*-isomers in the nitration of 3-phenylisothiazole[24] and the chlorosulphonation of 5-phenylisoxazole[135]; both compounds evidently react as the conjugate acids. In 4-phenylazoles the *para*- and *ortho*-positions of the benzene ring are the most active, and dinitro-derivatives are also readily formed[92,130,139].

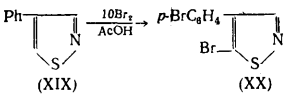
The presence of acceptor substituents in the heterocyclic ring of phenyl-azoles often changes the orientation of an incoming nitro-group[126,142]. Several papers have appeared[129,143,144] on substitution in arylazoles; among such reactions the nitration of 3- and 5-arylisoxazoles has been studied in the greatest detail[144]. With respect to ease of nitration aryl and heterocyclic substituents in arylazoles can be arranged in the sequence—fur-2-yl[145] > pyrazol-4-yl > phenyl $\simeq$ pyrazol-3(5)-yl > pyrazol-4-yl in the pyrazolium cation > isoxazol-4-yl > isothiazol-4-yl > *p*-nitrophenyl.

Halogenation. The nucleophilic character of the pyrazole ring is clearly developed during halogenation. Kinetic investigation of the iodination[146,147] and the bromination[148] of pyrazole and its methyl homologues has established that these compounds react as neutral molecules or conjugate bases. Isoxazole derivatives are halogenated in non-protonated form not only in acetic[2] but also in sulphuric[149] acid.

Treatment with molecular chlorine or bromine in water or an organic solvent yields 4-halogeno-derivatives of all 1,2-azoles[1,2,118]. With the less active isoxazoles and isothiazoles, however, the reaction is slow and incomplete. The iodination of 1,2-azoles, including pyrazole, goes similarly. The use of buffered solutions is sufficient to obtain 4-iodopyrazole[146,147], but the iodination of isoxazoles goes smoothly only in the presence of nitric acid[2]. Whereas in pyrazoles a halogen atom can be introduced at any position in the ring (to obtain trihalogeno-derivatives

it is convenient to use silver salts of pyrazoles[150]), with isothiazoles halogenation at positions 3 and 5 is exceptional[10,92]. Alkyl- and aryl-pyrazoles undergo thiocyanation at position 4 in the ring[151].

The greater selectivity of halogen molecules and ions than of the nitryl ion results in diverse products of the halogenation of phenylazoles. The aggregate effect of several factors—the activity of the halogen species, the electron density on the carbon atom involved, the energetic advantage of the transition state (intermediate compound)—probably determines the direction of attack. Complexes formed by azoles with halogens undoubtedly have an important role in halogenation. The process is most unambiguous with phenylisoxazoles: in all cases only 4-halogenoisoxazoles have been obtained, uncontaminated by isomers[2]. Among pyrazoles and isothiazoles examples are known in which halogenation occurs even in the benzene ring of the phenylazoles[92,152]:

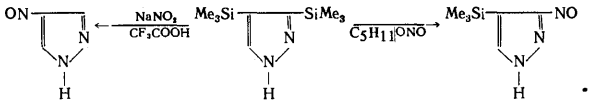


(XIX) (XX)

The bromination of phenylisoxazoles in aqueous acetic acid is a second-order reaction[153]. The activity of the isoxazole ring is significantly greater than that of benzene, and is determined by the nature and the position of substituents in the ring.

Other electrophilic substitutions. Pyrazoles and isoxazoles undergo hydroxy- and chloromethylation at the 4 position in the ring[1,2]. Carbonium ions, in contrast, attack the heterocycle at the nitrogen atom to form isoxazolium cations[154,155]. The highly nucleophilic character of the pyrazole ring is confirmed by the possibility of thermal and Friedel–Crafts acylation[1], and also Vilsmeier formylation[156]. Derivatives of isoxazoles do not undergo Friedel–Crafts acylation[157].

The presence of a labile carbon–silicon bond in a pyrazole derivative (XXI) enables a nitroso-group to be introduced at position 3 or 4 of the non-activated ring (XXII and XXIII):[158]



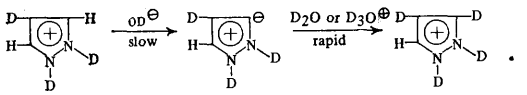
(XXIII) (XXI) (XXII)

Among isothiazoles only the 3,5-bismethylthio-derivative undergoes nitrosation[159].

(*b*) Protophilic substitution

At the present time protophilic substitution of hydrogen includes isotopic exchange in the presence of bases and metallisation by alkali-metal compounds[160]. The reactions involve intermediate formation of carbanions after detachment of a proton.

Only during recent years have studies been made on basic hydrogen exchange in pyrazole[122,161] and isothiazoles[10,162] catalysed by CH_3C^- and OD^- ions. The reaction involves the hydrogen atoms at positions 5 and 3. Isotopic exchange of the 5-proton in isothiazoles is a second-order reactions[162]. In the isothiazolium cation both protons are exchanged at high rates ($k \simeq 10$–6000 $M^{-1}\ s^{-1}$), but the 5-proton always the more rapidly[163]. Kinetic investigation of the deuteration of pyrazole has shown[161] that the reaction velocity is independent of the pD value; a mechanism with intermediate formation of an ylid was suggested:

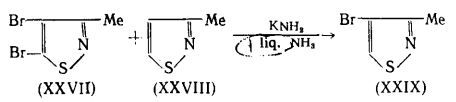


(XXIV) (XXV) (XXVI)

In pyrazole and isothiazole derivatives the 5-proton is always the most easily detached by n-butyl-lithium[10,164,165]. In monosubstituted isoxazoles strong bases attack the 3-proton first, and the resulting carbanion immediately rearranges into an open-chain enolate anion (see below). 3,5-Disubstituted isoxazoles containing functional groups (alkoxy, alkylthio, chloro) can be metallated at the 4 position[166,167].

The great reactivity of lithium derivatives of azoles has enabled many syntheses to be made. Organometallic synthesis is especially valuable for introducing various substituents at position 5 in the isothiazole ring[10,165,168], since the most widely used methods for obtaining isothiazoles yield 3- and 4-derivatives[10]. During this reaction such reactive groups as cyano and carboxy at position 4, as also halogen atoms, remain unaffected[10], which indicates the high kinetic acidity of the 5-proton in the isothiazole ring, and is fully consistent with kinetic data for isotopic hydrogen exchange.

The interesting migration of halogens from the 5 to the 4 carbon atom in 5-halogenoisothiazoles on treatment with potassamide in liquid ammonia is due to the greater stability of the isothiazol-5-yl than of the isothiazol-4-yl anion[169]. This was explained by a five-stage mechanism, supported by the quantitative debromination of the 4,5-dibromoisothiazole (XXVII) by the unsubstituted compound (XXVIII) to the 4-bromoisothiazole (XXIX):



(XXVII) (XXVIII) (XXIX)

A similar mechanism to the above reactions underlies that reported by Begtrup between pyrazolium salts and sodium hydride in the presence of oxygen or sulphur, with intermediate formation of an ylide of type (XXV) to yield pyrazolones or pyrazolethiones respectively[170,171].

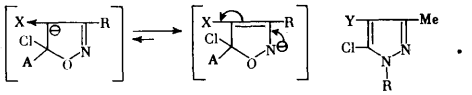
(*c*) Nucleophilic substitution

Reactions involving nucleophilic substitution by an S_N2 mechanism have been reported mainly for halogeno-derivatives of 1,2-azoles. In contrast to the inert 3- and 5-halogenopyrazoles and 5-halogenoisothiazoles, the isoxazole analogues undergo such reactions when heated to 100°C.[2,172] A 3-nitro-group in isoxazoles is also readily substituted by hydroxy- and alkoxy-groups[173,174]. Reaction with copper(I) cyanide has great value for the preparation of isothiazole derivatives; 5-bromoisothiazoles react more readily than do the 4-isomers[10].

Introduction of an electron-accepting 4-substituent increases appreciably the mobility of a 5-halogen, especially in the isoxazole ring[1,2,10,118,175,176]. Even the two nitro-groups in 4-bromo-1-methyl-3,5-dinitropyrazole activate the halogen atom[131] far more weakly than the benzoyl substituent in 4-benzoyl-5-chloroisoxazoles[2].

The ^1H n.m.r. spectra of 4-nitro-azoles indicate that unreactive molecules have approximately equal electron densities on the 5-carbon atom. Therefore the decisive

factor for easy occurrence of S_N2 reactions in the isoxazole series should be a lower activation energy, whose magnitude is undoubtedly governed by formation of the transition state (XXX). Isomerisation of the carbanion (XXX) into the energetically favourable anion (XXXI) is promoted by strong polarisation of the nitrogen–oxygen bond in the heterocycle:



(XXX) (XXXI) (XXXII)

Nucleophilic substitution takes place readily also in 3-halogenoisoxazolium [177] and 3- and 5-halogenopyrazolium [178] cations.

Kost and Grandberg [1] studied the kinetics of the action of excess of hexamethyleneimine on 5-chloropyrazoles of type (XXXII). Under the given conditions the reaction was pseudounimolecular. The influence of substituents Y diminishes in the sequence

$$NO_2 \gg C_6H_5N : N > C_6H_5CO \gg Br > H .$$

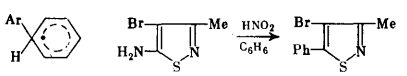
(*d*) Homolytic substitution

Arylation. It was established during the 1960s that arylation takes place by the same mechanism involving a σ complex (XXXIII) independently of the source of the radicals. Results obtained on the phenylation of 1-methyl- and 1-phenyl-pyrazoles and of isothiazole and its methyl homologues have been summarised in a French review on the homolytic arylation of heterocycles [179]. Decreasing rates of phenylation in a neutral medium give the sequence

$$\text{4-MeIth } (1.85) > C_6H_6\ (1) \simeq \text{Ith } (0.95) > \text{3-MeIth } (0.65) \simeq \text{1-MePyr } (\sim 0.6) > \text{5-MeIth } (\sim 0.3)$$

where Ith and Pyr represent isothiazolyl and pyrazolyl respectively. Individual positions in the heterocyclic ring differ greatly in activity: in isothiazole the carbon atoms 3 and 5 are attacked by the phenyl radical five times as frequently as carbon atom 4; in 1-methylpyrazole attack occurs almost exclusively at position 5. In *N*-phenylpyrazole reaction occurs to ~55% at the *ortho* position of the benzene ring and 30% at the 3-carbon atom of the pyrazole.

The reverse reaction to arylation—attack on aromatic compounds by azolyl radicals—has been reported in several papers [180–182]. Such a reaction has been used [10] to obtain 4- and 5-phenylisothiazoles from the corresponding amines, e.g. (XXXV) from (XXXIV):



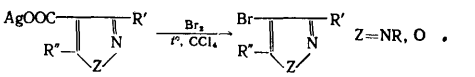
(XXXIII) (XXXIV) (XXXV)

Organometallic compounds from halogeno-azoles. During the past decade a radical mechanism has been firmly established by various methods for the reaction of halogeno-derivatives with magnesium, and also for the exchange of organo-magnesium and -lithium compounds with halides, which occurs "in a cage".

Halogeno-derivatives of pyrazole and isoxazole do not react with magnesium except in the form of another Grignard reagent [1,2]. The activities of halogenopyrazoles fall in the sequences 5-Hal > 4-Hal >3-Hal and I > Br > Cl. [1] The same rules apply to isoxazole derivatives [2,183], with the exception of 5-halogenoisoxazoles, whose reactivities have not been finally elucidated. As noted above, pyrazol-5-yl- and isothiazol-5-yl-lithium can be obtained by direct metallisation. Exchange therefore finds application in the preparation of 4-derivatives of pyrazole [1] and isoxazole [184] that cannot be obtained in other ways, e.g. 4-deuteroisoxazoles.

Other homolytic reactions. Diazo-reactions, which probably occur by a radical mechanism, have proved especially important for obtaining 5- and 4-halogenoisothiazoles by the Sandmeyer reaction [10]. During recent years 3(5)-halogeno-derivatives of pyrazole and isoxazole have been obtained by the diazo-reaction; for the reaction to proceed normally the ring must contain electron-accepting substituents, which enhance the stability of the diazo-compounds [185–187].

The Borodin–Hunsdecker reaction also takes place by a free-radical mechanism. It has been used to convert *N*-substituted pyrazole-4(5)-carboxylic [1,152] and isoxazole-4-carboxylic [188] acids into bromo-derivatives:



(XXXVI) (XXXVII)

The isomeric pyrazole-3-carboxylic acids do not react, and isoxazole-3(5)-carboxylic acids decompose [188]. Isoxazol-3(5)-yl radicals are probably unstable, and isomerise with cleavage of the ring [189].

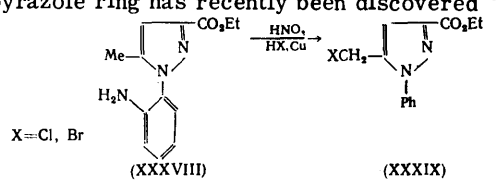
2. Substitution in a Side-chain

(*a*) Preparation and reactions of halogeno-derivatives

Two different methods—halogenomethylation and the halogenation of methyl groups—can be used to obtain halogenomethyl-azoles, which find widespread application for the preparation of various derivatives. The latter method can be regarded as effective only for the selective introduction of one or two halogen atoms. Therefore chlorination in acetic acid is not employed for this purpose, for it yields mixtures of chloro-derivatives of pyrazole [1] and isoxazole [190]. In polymethyl-azoles methyl groups are completely chlorinated at positions 5 and 3, but not at 4. This reaction must therefore be regarded as electrophilic substitution at a saturated carbon atom.

N-Bromosuccinimide, which reacts by a radical mechanism, is most convenient for obtaining monohalogenomethyl-azoles. Great differences in the activity of methyl groups are observed depending on the nature of the heterocycle, the position of the groups in the ring, and other substituents. The reactivity of methyl groups in different positions in isoxazole derivatives falls in the sequence $C_{(4)} > C_{(5)} \gg C_{(3)}$; [2,191] the reaction is completely inhibited by strong acceptors of electrons (nitro, benzoyl). In the isothiazole series, on the other hand, a 3-methyl group is highly active: mono-, di-, and tri-bromo-derivatives can be obtained by the action of *N*-bromosuccinimide, with no bromination of the heterocyclic ring [10,192].

An unusual homolytic halogenation of a 5-methyl group in the pyrazole ring has recently been discovered [193]:

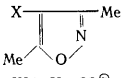


(XXXVIII) (XXXIX)

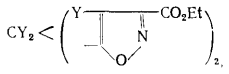
Nucleophilic substitution of the halogen atom in halogenomethylated azoles has been used to obtain physiologically active compounds, especially amines, in the isoxazole [2,194] and isothiazole [10,195] series. Dihalogenoazoles are converted smoothly into aldehydes either by direct hydrolysis or with preliminary formation of intermediate products [2,10,196].

(*b*) Protophilic substitution

Isotopic hydrogen exchange. Such exchange in the presence of bases has been studied mainly in azoles containing methyl groups and acceptor substituents in adjacent positions. Deuterium exchange catalysed by the OD^- ion has been accomplished [10] only in methylisothiazoles. The activity of methyl groups falls in the sequence of positions 5 ≫ 3 > 4, with relative rate constants $10^2 : 1 : 10^{-4}$. In the isoxazole series deuterium exchange in methyl groups has been investigated in the 4-substituted 3,5-dimethylisoxazoles (XL)–(XLII) [197,198] and in diethyl methanebis-5-isoxazole-3-carboxylate (XLIIIa) [199]



(XL), X = $CO_2^{\ominus}$;
(XLI), X = C_6H_5N : N
(XLII), X = NO_2;

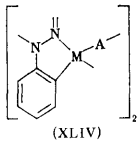


(XLIII) a) Y = H,
b) Y = D

Under the most severe conditions (catalysis by the OD^- ion) reaction occurs in the carboxylate anion (XL). Isotopic hydrogen exchange is greatly facilitated in compounds (XLI) and (XLII), and the rate could not be measured for the reaction of the nitroisoxazole (XLII) with *N*-deuterodiethylamine. Entry of deuterium into the 5-methyl groups was demonstrated by ^1H n.m.r. spectroscopy for all three compounds. Only the ^1H n.m.r. spectrum will reveal instantaneous deuterium exchange in compound (XLIIIa), which yields (XLIIIb) via methineisoxazoles.

Metallation. The metallation of methyl groups by butyl-lithium and organometallic synthesis from the resulting lithium derivatives have been reported in the isoxazole [165,166,200–203] and pyrazole [164,165] series. In methylisoxazoles a 5-methyl group always reacts, being more active than the 4-proton, but in methylpyrazoles an *N*-methyl group reacts. The influence of the 1-heteroatom is clearly evident here: it carries a definite positive charge, and governs the kinetic acidity of adjacent protons. In pyrazole derivatives the activity of individual positions and substituents diminishes in the sequence 5-H > *N*-C_6H_5 > *N*-CH_3, 5-CH_3 ≈ 5-Cl.

In contrast to methylpyridines, in which selective metallation can be achieved by the use of various reagents, 3,5-dimethylisoxazole reacts with any strong base only at the 5-methyl group. Treatment with metal amides followed by alkyl halides gives good yields of 5-n- and 5-iso-alkylisoxazoles [204], as well as di- and tri-isoxazolylalkanes [205].



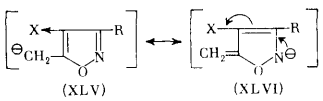
(XLIV)
M = Pd, Mn, Rh, Ir

During recent years selective metallation of *N*-phenylpyrazole in the *ortho*-position of the benzene ring has been accomplished not only with ethylmagnesium bromide [206] but also with compounds of heavy metals [207–209], which gives rise to intramolecular complexes of type (XLIV).

Condensation. Most of the condensation reported for methyl derivatives of 1,2-azoles are catalysed by bases and can also be included among protophilic substitutions (for the condensation of 5-methylisothiazole in acetic anhydride see review [10]). Selective activation of a 5-methyl group is achieved in the presence of an electron-accepting substituent at position 4 in the heterocycle. The most marked effect is observed among the isoxazole derivatives (XL) and (XLII); the catalysts and conditions of condensation are similar to those discussed above for deuterium exchange [2,210]. 5-Methyl-4-nitroisothiazoles react with aldehydes under more severe conditions [10], but 3,5-dimethyl-4-nitropyrazole does not condense at all with aldehydes in the presence of amines [1].

Michael addition of activated methylene and methyl groups in isoxazole derivatives has also been described [2,199]. In 1,2-azolium cations 3-methyl groups are also active [1,2].

Results for protophilic substitution in methyl groups indicate that 5-methylisoxazoles tend to form isoxazol-5-ylmethyl anions (XLV). This occurs especially readily in the compounds (XL)–(XLII), in which X is an electron-accepting substituent. They obviously contain a localised $C_{(4)}=C_{(5)}$ bond, which transmits the effects of substituents. However, the low activation energy, associated with resonance stabilisation of the resulting carbanion



(XLV) (XLVI)

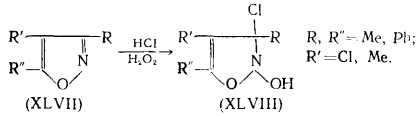
is probably the decisive factor in the ready occurrence of protophilic substitution.

3. Addition to the Heterocyclic Ring

Reactions involving addition have been studied far less thoroughly than those involving substitution. Here we shall consider only reactions which enable di- and tetrahydro-derivatives to be obtained, as well as those in which isomerisation into 3*H*- or 4*H*-pyrazoles takes place.

(*a*) Electrophilic addition

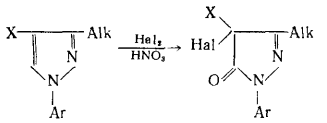
In 1964 Sokolov and Kochetkov described the first reaction involving addition to the isoxazole ring [211,212], in which hypochlorous acid adds at the $C_{(3)}-N$ bond of the heterocycle (XLVII) to form 3-chloro-2-hydroxy-Δ^4-isoxazolines (XLVIII):



(XLVII) (XLVIII)

R, R″ = Me, Ph;
R′ = Cl, Me.

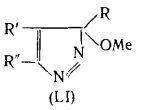
Under corresponding conditions 3-alkyl-*N*-(2,4-dinitrophenyl) pyrazoles react with hypohalous acids at the $C_{(4)}=C_{(5)}$ bond with intermediate formation of 4-halogeno-5-hydroxy-Δ^2-pyrazolines, which undergo further oxidation to the pyrazol-5-ones (L):[213,214]



(XLIX) (L)

Ar=2,4-$(O_2N)_2C_6H_3$; X=Br, Cl, Me; Hal=Br, Cl.

The unstable structure of 4-alkyl-4-bromopyrazoles is confirmed by ^{1}H n.m.r. spectroscopy for products of the reaction of 3,4,5-trialkylpyrazoles with bromine or *N*-bromosuccinimide[215,216]. In the presence of methanol 3*H*-pyrazole derivatives



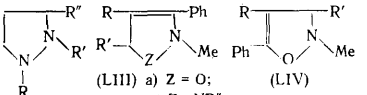
(LI)

are formed.

In all the above reactions the attacking halogen-containing species are evidently electrophilic. Dichlorocarbene, which is also an electrophile, reacts with the ring of 3,4,5-trimethylpyrazole to give a whole range of products, including a quite stable 4*H*-pyrazole derivative[217].

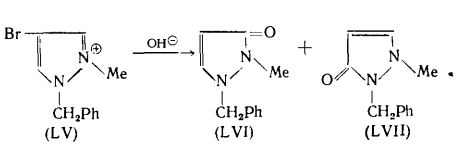
(*b*) Nucleophilic addition

Like quaternary salts of various nitrogen heterocycles 1,2,3-substituted pyrazolium and isoxazolium cations readily add hydride ions. Sodium tetrahydroborate reduces pyrazolium ions to pyrazolidines (LII),[218-220] whereas reduction of isoxazolium ions usually halts at the stage of formation of Δ^3- and Δ^4-isoxazolines (LIIIa) and (LIV).[221] Δ^3-Pyrazolines (LIIIb) can be obtained by means of lithium tetrahydroaluminate[218]. Adachi et al.[222,223] have been able to add carbanions from organomagnesium compounds to 3*H*- and 5*H*-isoxazolium ions at 0°C to form (LIIIa) and (LIV). Under the same conditions secondary amines also add to the 5-carbon atom in the 5*H*-isoxazolium ion[222].



(LII) (LIII) a) Z = O; b) Z=NR". (LIV)

An interesting reaction involving addition and elimination begins with attack by the hydroxide ion at positions 3 and 5 in the cation (LV) followed by detachment of hydrogen bromide to give the pyrazol-3- and -5-ones (LVI) and (LVII):[224]

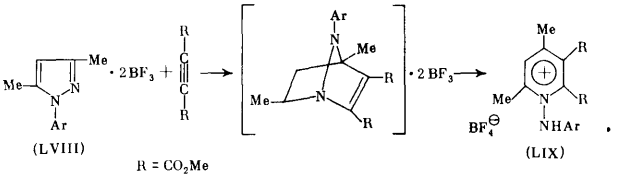


(LV) (LVI) (LVII)

(*c*) Molecular addition

Catalytic hydrogenation, which can be regarded as a homolytic process, yields di- and tetra-hydro-derivatives only in the case of pyrazoles[1]: the isoxazole and isothiazole rings undergo hydrogenolysis under these conditions (see below). Electrochemical reduction of the $C_{(4)}=C_{(5)}$ bond in the pyrazole ring has also been described[225].

In 1974 the possibility was discovered of effecting diene synthesis in the pyrazole series, catalysed by boron trifluoride[226]:



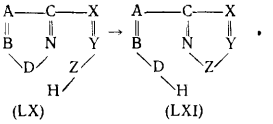
(LVIII) R = CO_2Me (LIX)

IV. REACTIONS WITH CLEAVAGE OF HETEROCYCLIC RING

Reactions of isoxazole derivatives accompanied by cleavage of the heterocyclic ring have found widespread application in organic synthesis. The numerous publications on this topic have been systematically surveyed in the reviews of Nishiwaki[3] and Subrahmanyam[4], which are complementary: the former covers syntheses of various heterocycles based on isoxazoles, and the latter the preparation of peptides and carbocyclic systems, including steroids and terpenes. The following account will make considerable use of these reviews, with references only to the main publications covered, as well as to papers that have appeared since.

1. Rearrangement

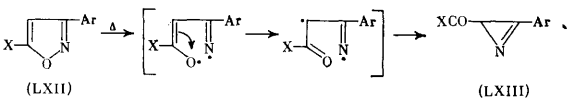
Rearrangements of isoxazole derivatives, the greatest contribution to whose study has been made by Adachi and Kano[3], had already become known by the end of the 1930s. More recently data have been summarised[227] on one of the rearrangements, termed[227] "monocyclic" and occurring under the influence of bases:



(LX) (LXI)

The conversion of isoxazoles into furazans, 1,2,3- and 1,2,4-triazoles, and tetrazoles takes place by the same mechanism.

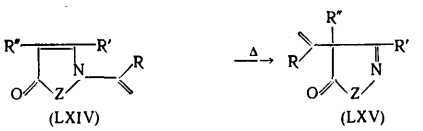
Nishiwaki made a detailed study of the thermal isomerisation of isoxazoles (LXII) containing alkoxy, alkylthio, or amino at the 5 position[3]. In contrast to 3,5-dialkyl(or aryl)isoxazoles these compounds are converted at 150–230°C into azirine derivatives (LXIII):



(LXII) (LXIII)

Komendantov and Bekmukhametov have discovered a catalytic isomerisation of 5-methoxy-3-phenylisoxazole[228], for which they suggest homolytic fission of the nitrogen–oxygen bond with intermediate formation of biradicals[3], which is supported by kinetic results[228]. Reactions of (LXII) with arylamines and trialkyl phosphites also involve formation of azirine derivatives[3].

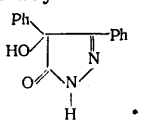
N-Allyl-azol-5-ones (LXIV) when heated undergo an amino-Claisen rearrangement through a cyclic transition state into 4-allyl-azolones (LXV),[229,230] with inversion of the allyl group:



(LXIV) (LXV)

Z=NPh, O

Among alkali-catalysed rearrangements note must be taken of the acyl–lactone rearrangement of 4-acylisoxazol-5-ones [2,231] and the oxidation of 4-hydroxy-3,5-diphenylpyrazole to the acylion [232]



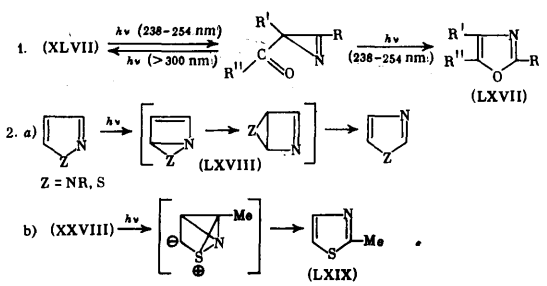
(LXVI)

The mechanism of the latter complicated process has not yet been established.

The lability of the isoxazole ring is evident also in the rearrangement accompanied by fragmentation occurring when di(or tri)alkylisoxazoles are treated with diphenylcyclopropenone [3].

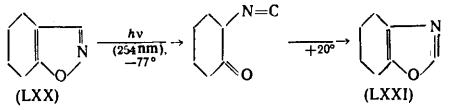
2. Photolytic Isomerisation

Whereas heating and chemical reagents cause rearrangement mainly of isoxazole derivatives, exposure to ultraviolet radiation causes the isomerisation of all 1,2-azoles, on which the first publications appeared during the mid-1960s. From the vast quantity of information that has now accumulated we must single out results on the isomerisation of pyrazoles [233,234], isoxazoles [3,235], and isothiazoles [236–238]. Photorearrangements of 1,2-azoles can occur in two ways—(1) ring contraction–expansion (XLVII) ⇌ (LXVII) [3] or (2) ring isomerisation through (*a*) bicyclic transition states (LXVIII) or (*b*) intermediate zwitterions (XXVIII) → (LXIX):



Isomerisation of pyrazoles into imidazoles sometimes also follows the first route [234], but such rearrangement usually takes place according to Scheme 2*a*. [233,234] Modes of transition of isothiazoles into thiazoles are the most diverse, owing to the tendency of the sulphur atom to form a sulphonium ion, but path (1) is not followed at all by isothiazoles.

The course of the photoisomerisation of 1,2-azoles may vary depending on the nature and the position of substituents in the heterocycles. Thus, whereas 5-amino-3-phenylisoxazoles are converted into the corresponding oxazole derivative, aminoisoxazoles unsubstituted at the 3 position rearrange into acyclic compounds [3]. Photoinduced attack by the solvent on intermediate products of the isomerisation of isoxazoles also yields polyfunctional acyclic compounds [3,239]. In 1973 a novel photoisomerisation was discovered, of the isoxazole (LXX) into the oxazole (LXXI) via a β-keto-isocyanide [3]:

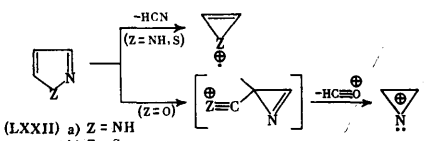


(LXX) (LXXI)

As a result of photoinduced redox reactions *N*-*o*-nitrophenylpyrazoles are converted into *N*-oxides of benzotriazoles [240].

3. Mass Spectra of 1,2-Azoles

The first bonds to break under mass-spectroscopic conditions are the most unstable, which in 1,2-azoles are those between the heteroatoms. Indeed, the most intense peaks in the mass spectra of the unsubstituted azoles



(LXXII) a) Z = NH
b) Z = S
c) Z = O

are due to the molecular ions and the $[M-HCN]^+$ ions for pyrazole [241,242] and isothiazole [243] or $[M-HCO]^+$ ions for isoxazole [244]. Removal of the ring carbon atom 3 (or 5) has been proved [242] for such fragmentation of pyrazole. The molecular ion of isoxazole (LXXIIc) is the least stable [244]. As with other isomerisations, an intermediate azirine derivative (LXIII) is formed here. Conversion of 5-substituted isoxazoles into azirine derivatives under the influence of electron bombardment has been studied by Nishiwaki [245] in comparison with corresponding thermal and photoinduced isomerisations.

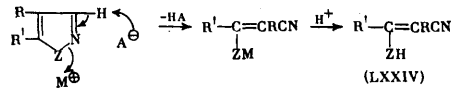
Differences in behaviour are observed between *C*-methyl homologues of pyrazole and isothiazole and of isoxazole: whereas in the first two series a hydrogen atom is removed from the methyl groups of the molecular ions with the formation of six-membered rearranged ions [61,241,243], the molecular ions of methylisoxazoles first undergo rupture of the cyclic nitrogen–oxygen bond [246]. The position in the ring of the substituent in the isomeric monomethylisothiazoles can be determined from the mass spectra [243]. In contrast, the peaks due ionic fragments in the mass spectra of three dimethylpyrazoles differ only in intensity [241]. The stability of the pyrazole ring on electron impact (the quantity W_M) falls in the sequence pyrazole > 1-methylpyrazole > 3(5)-methylpyrazole.

The fragmentation of phenyl derivatives has been discussed in several papers [184,243,247,248]. Isomeric arylphenylisoxazoles can easily be distinguished by their mass spectra [249].

4. Nucleophilic Cleavage

The numerous studies of various aspects of the nucleophilic cleavage of 3*H*-isoxazoles (LXXIIIa) and of the 5*H* isomers, which was discovered as early as 1891, have been summarised in reviews [2,7,8]. Nucleophilic fission of the pyrazole ring unsubstituted at the 3 position (LXXIIIb)

is possible under severe conditions [250,251]. The scission products of isoxazoles and pyrazoles are respectively β-keto-nitriles (LXXIVa) and β-aminoacrylonitriles (LXXIVb):



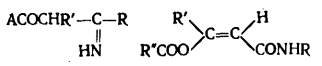
(LXXIII) a) Z = O, b) Z = NR
M = Na, K; A = OH, OR'' .

The products (LXXIVa) are used in organic synthesis [2,4,154].

Electron-acceptor substituents diminish the electron density on the 3-carbon atoms and facilitate nucleophilic cleavage. Thus potassium t-butoxide affects ring opening only in 1-phenylpyrazoles containing benzoyl, cyano, or toluene-*p*-sulphonyl at position 4.

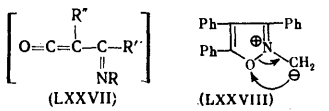
Pino et al. established the mechanism of the cleavage of isoxazoles [2,252]. Overall the reaction has kinetic second order; for the isomerisation of 5-arylisoxazoles a good correlation has been found between $\lg K$ and σ ($\rho = 0.51$, $r \simeq 1$). The nucleophilic cleavage of pyrazoles probably has the same mechanism.

3,4-Disubstituted isoxazoles open with greater difficulty in the presence of bases; 5-methylisoxazole cleaves more rapidly than the 3-isomer [252] by a factor of 14. A review [2] has given different decomposition paths for such compounds, which depend on the stability of the intermediate product (LXXV).



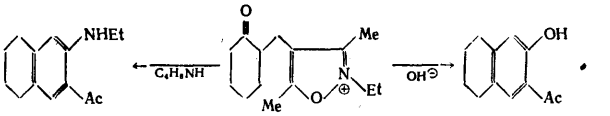
(LXXV) (LXXVI)

In isoxazolium and isothiazolium cations the acidity of the 3-protons has so increased that ring cleavage takes place under mild conditions. 2-Alkylisothiazolium salts on treatment with hydroxide ions at 20°C break down with the formation of resins [253]. The action of weaker nucleophiles is often accompanied by recyclisation into 1,2-azoles [10]. Ring opening takes place in 3*H*-isoxazolium ions even under the influence of carboxylate anions. The true mechanism of this multistage reaction was established by Woodward and Olofson by spectroscopic methods [254]. The enolic esters (LXXVI) formed during the reaction, which possess strong acylating power, have found application in the synthesis of peptides [4,255,256] and nucleotides [257] and in the modification of enzymes [258]. These esters are easily reduced by sodium tetrahydroborate, which forms the basis of a new method for preparing alcohols from acids [259].



(LXXVII) (LXXVIII)

Cleavage of 5*H*-isoxazolium can occur either in the presence of a strong base with detachment of the 5-proton and formation of the keten (LXXVII) or with addition of a weaker base (phenylhydrazine) to the 5-carbon atom followed by transcyclisation [3]. In the case of tetrasubstituted isoxazolium ions the direction of ring opening and subsequent reactions is determined by the nature of the substituents. Treatment of 2-methyl-3,4,5-triphenylisoxazolium with alkali forms 4,5,6-triphenyl-2*H*-1,3-oxazine, presumably via the ylid (LXXVIII). [2,3] Transformation of the heterocycle in the cation (LXXIX) has a completely different course: this compound can be selectively converted into functional derivatives of tetralin (LXXX) and (LXXXI): [4,260]

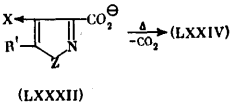


(LXXX) (LXXIX) (LXXXI)

This reaction has been used also for the synthesis of terpenes [260].

Ring opening is probably a consequence of attack by the base on the nitrogen atom. A similar cleavage mechanism—nucleophilic substitution at the sulphur atom—is assumed for the action of butyl-lithium on (XXVIII). [10,165]. The sulphur–nitrogen bond in 3-hydroxyisothiazoles has proved very labile: it is broken not only by carbanions but also by cyanide ions [10]. The ring in 3-chloro-4-nitroisothiazole is also opened by amines [261].

The decarboxylation of isoxazole-3-carboxylic acids is akin to nucleophilic ring cleavage in 3*H*-isoxazoles, since the same β-keto-nitrile products (LXXIVa) are formed. No special investigation has been made of the reaction mechanism, but intermediate formation of a zwitterion can be assumed [2]. The carboxylate anions formed in solution or in the presence of arylhydrazines are decarboxylated under milder conditions:



(LXXXII)

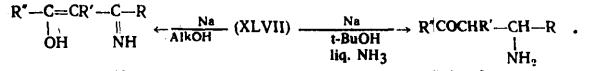
a) Z = O; b) Z = NPh; X = R .

The presence of an electron-accepting 4-substituent in the acid (LXXXIIa) so facilitates decarboxylation that it occurs even on alkaline hydrolysis of the esters; this reaction was used by Woodward et al. in synthesising polycondensed systems [4]. In boiling quinoline ring cleavage takes place even in the pyrazole analogues (LXXXIIb). [262]

5. Reductive and Oxidative Cleavage

The labile nitrogen–oxygen bond in the isoxazole ring is ruptured by very many reducing and oxidising agents. The behaviour of isoxazole derivatives is determined by the reaction conditions and the comparative activities of this bond and multiple bonds in a side-chain. In the absence of functional groups in a side-chain, for example, even lithium tetrahydroaluminate destroys the isoxazole ring [263]. An exocyclic double bond, on the other hand, can be subjected to ozonolysis without affecting the heterocycle [264].

Reductive cleavage of alkali-stable 3,4,5-trisubstituted isoxazoles (XLVII) by the action of sodium in alcohols yields β-imino-ketones (LXXXIII), [2] but reaction with t-butyl alcohol in liquid ammonia gives β-amino-ketones (LXXXIV): [265]

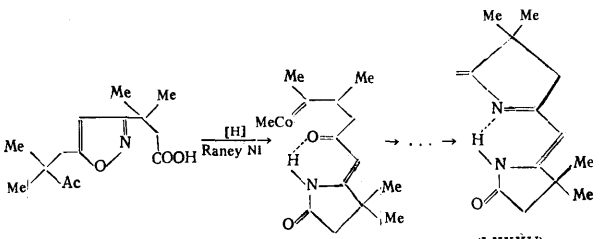


(LXXXIII) (LXXXIV)

Vinyl ketones [266] and β-diketones [204,205] can also be obtained.

It has been established during recent years that the acidity of the medium is a decisive factor in the selective hydrogenation of alkenylisoxazoles. Use of palladium as

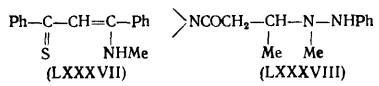
catalyst in an acid medium enables hydrogenation to be confined to the double bond in the side-chain[260,267]. In an alkaline medium, on the other hand, the cyclic nitrogen–oxygen bond is easily ruptured[4,268]. Applying this reaction to 4-chloromethylisoxazoles[269], Stork et al. developed a method for building up cyclohexanone rings in polycyclic systems[4] and used it to accomplish a complete synthesis of *dl*-*D*-homotestosterone[4,270]. The method of annellation has been further developed for the synthesis of steroids by Scott et al.[268,271,272] Numerous carbocyclic[4,273-275] and heterocyclic[3] systems have also been obtained from the hydrogenolysis products. An elegant method for obtaining semicorrins (LXXXV), devised by two groups of chemists[276,277] using the same polyfunctional isoxazole derivative (LXXXVI) as starting material,



(LXXXVI) (LXXXV)

can rightly be regarded as a great success for this trend in the synthetic use of isoxazoles. The electrochemical reduction of phenylisoxazoles, in contrast to that of pyrazoles, also leads to rupture of the heterocyclic nitrogen–oxygen bond[278].

Individual products cannot be obtained by the catalytic hydrogenation of isothiazole derivatives[10]. On the other hand, the 2-methyl-3,5-diphenylisothiazolium ion can be easily reduced by benzenethiol to the 2-aminovinyl thioketone (LXXXVII).[253] 5-Amino-2-methyl-1-phenylpyrazolium cations are reduced by lithium tetrahydroaluminate with rupture of the $N_{(1)}-C_{(5)}$ bond to β-hydrazino-amides (LXXXVIII).[219]



(LXXXVII) (LXXXVIII)

The course of the oxidation of 1,2-azole derivatives depends on the nature of the rings and the substituents. Pyrazoles and isothiazoles are quite stable when heated with alkaline potassium permanganate, so that this method can be widely used to obtain azolecarboxylic acids[1,10]. The cleavage of the isoxazole ring under these conditions has been used to establish orientation on electrophilic substitution in arylisoxazoles[2].

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During preparation of the manuscript for press several important publications have appeared—on the physical and physicochemical properties of 1,2-azoles[279-283], substitution in ring and side-chain[284-296] and addition to double bonds in azoles[297-299], and ring cleavage with syntheses based on the cleavage products[300-304] (the sequence of topics in this list corresponds to the treatment in the Review).

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Electrochromism for the Investigation of Slow Movements in Macromolecules

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An account is given of the most important theoretical principles of electrochromism, and the possibility of its application is discussed. Apparatus and method of measurement are described. Results are considered for linear polymers in elastic and vitreous states over the range of relaxation times 10^{-3} - 10^{6} s. A list of 31 references is included.

CONTENTS

I.	Introduction	306
II.	The phenomenon of electrochromism	306
III.	Investigation of amorphous polymers in vitreous-elastic transition range by quadratic electrochromism	310
IV.	Study of elastic state of amorphous polymers by quadratic electrochromism	312
V.	Investigation of vitreous state of amorphous polymers by linear electrochromism	313
VI.	Experimental procedure	314

I. INTRODUCTION

Use of especially sensitive apparatus reveals that an external electric field deforms absorption bands associated with solutions of organic molecules. This phenomenon occurs throughout the solution and is caused by interaction between the solute molecules and the field. Such interaction is apparent in the absorption spectra as optical anisotropy of the medium—dichroism of the solutions—and as spectral shifts in the bands caused by Stark effects. The broad absorption bands of complicated organic molecules exclude the possibility of applying the techniques of observation and interpretation that have been developed in studying Stark effects on line emission spectra. Some authors therefore consider it advisable to apply the term *electrochromism* to the deformation of molecular absorption bands in solution. The most complete description of electrochromism will be found in the works of Liptay, who as early as the 1960s suggested its use as a method for determining molecular excitation parameters[1].

Our work has shown[2-4] that electrochromism has another use—to study slow molecular mobility in condensed media, in particular in polymers—for which purpose molecules are introduced into the test medium to act as probes, and their rotational movements are observed by means of electrochromism. As in all other probe methods for studying molecular dynamics, it is in turn assumed that movements of the probes are determined solely by the thermal motion of molecules of the medium.

An obstacle to investigating slow movements by the paramagnetic probe method[5] is the so called relaxation conditions, which imposes a lower frequency limit at 10^{-7} s. During recent years paramagnetic probe methods have been devised in which the frequency limit has been lowered to 10^{-4} s.[6] An advantage of electrochromism over paramagnetic probes is the absence of theoretical limits in the low-frequency region. We have investigated molecular mobility in polymers between 10^{-3} and 10^{6} s. The approximately six frequency ranges thus covered are typical of the vitreous state. A relaxation time of 10^{6} s corresponds to a period of ~2 weeks, but this does not mean that such is the lower frequency limit of the method. The hypothetical possibility remains of using electrochromism to study even infinitely long relaxation processes. On the other hand, extending the range to short times (10^{-5}–10^{-6} s) leads merely to fully surmountable technical difficulties. There was no need in our work to raise the frequency, firstly because the dielectric method and the paramagnetic probe method are successfully used in the respective ranges 10^{-1}–10^{-10} and 10^{-7}–10^{-8} s, and secondly because the low-frequency range is the most interesting and promising, for it characterises mainly the relaxation processes that govern the properties of most polymer materials.

Electrochromism, like the Stark effect, is due to orientation polarisation of the probe molecules, which makes it akin to dielectric methods for investigating molecular mobility. The advantages of electrochromism are due to its high selectivity: since the method is based on observing the absorption spectra of probes, measurement can be confined to their orientational mobility, and other types of polarisation of the medium, which make a contribution in dielectric measurements, can be excluded.

Electrochromism can in principle be studied using probes that have been grafted on or even included in the main polymer chain. Another possible and extremely promising method of measuring inherent absorption involves observing that of chromophoric groups in the macromolecule, and directly determining their mobility. For the majority of polymers such investigation are possible only in the far ultraviolet.

II. THE PHENOMENON OF ELECTROCHROMISM

The action of an electric field on an absorption spectrum was first detected experimentally in 1939 by Kuhn et al.[7] for nitrosodimethylaniline dissolved in dioxan. Kuhn suggested that considerable orientation polarisation of the dissolved dipolar molecules might be produced in a strong electric field of $\sim 10^{4}$ V cm^{-1}. Since there is a fixed angle γ between the directions of the dipole moment of the molecule in the ground state $\bar{\mu}_g$ and that of the transition moment (unit vector $\bar{m}$), under certain conditions the orientation polarisation of the moments $\bar{\mu}_g$ may

be accompanied by anisotropy in the distribution of transition moments observable by means of special apparatus, together with dichroism of the solution. The optical density measured by means of a light ray parallel to the field strength vector $\bar{F}$ then differs from that measured perpendicular to this direction. The aim of the early work[7] was to evaluate the angle γ in organic molecules from the experimental dichroism.

Considerably later Labhart[8], Czecalla[9], and mainly Liptay and his coworkers[10] established that in Kuhn's experiments the expected orientation effect was accompanied by other effects, resulting from Stark displacements of the energy levels of ground and excited electronic states of the molecules. The shift in the levels is determined by interaction of a molecule possessing dipole moments $\bar{\mu}_g$ and $\bar{\mu}_e$ and polarisability tensors α_g and α_e with the external field (here and subsequently the subscripts g and e denote ground and excited states respectively). Furthermore, Liptay subsequently examined the action of a field on the transition moment of the molecules, and showed that this effect is also included in the observed electrochromism[1].

We consider the absorption of light by one of the molecules in the ensemble under investigation, whose orientation relative to the vector $\bar{F}$ is rigidly fixed. The shift in the absorption band in the field is determined by the displacement of the ground and excited electronic levels. Fig. 1 illustrates how the mutual arrangement of the vectors $\bar{\mu}_g$, $\bar{\mu}_e$, and $\bar{F}$ influences (disregarding the contribution of polarisability) the magnitude and the direction of the spectral shift in the bands (which for clarity has been greatly exaggerated).

From the above considerations the shift of the band in the field can be calculated by means of the formula

$$\Delta\bar{\nu} = \bar{\nu}^0 - \bar{\nu}^F = -\frac{\bar{\mu}_e - \bar{\mu}_g}{hc}\bar{F} - \frac{1}{2hc}(\alpha_e - \alpha_g)\bar{F}^2$$

where $\bar{\nu}^0$ and $\bar{\nu}^F$ are wave numbers of the electron transition in the absence and in the presence of the field, h is Planck's constant, and c is the speed of light. Writing $\Delta\bar{\mu} = \bar{\mu}_e - \bar{\mu}_g$ and $\Delta\alpha = \alpha_e - \alpha_g$, we obtain

$$\Delta\bar{\nu} = \frac{\Delta\bar{\mu}\bar{F}}{hc} + \frac{\Delta\alpha\bar{F}^2}{2hc} \quad (1)$$

In the maximum practicable fields (10^5 V cm^{-1}) the shift in the bands is a fraction of an Ångström unit under optimum conditions. Direct measurement of such small shifts in wide spectral bands is an extremely complicated task, so that measurements are made not of the band shifts but of the increase in luminous flux at a fixed wave number due to the action of the field. According to Eqn. (1) in an electric field transitions will be observed at a wave number $\bar{\nu}$ that are observed at wave number $\bar{\nu}-\Delta\bar{\nu}$ in the absence of a field. A low-frequency alternating field is usually applied to the specimens, and only the modulated part of the luminous flux, due solely to electrochromism, is measured.

The absorption of light by one molecule in the absence of a field is[11]

$$\pi(\bar{\nu}) = 3|\bar{e}\bar{m}|^2 \epsilon(\bar{\nu})/\bar{\nu},$$

where $\bar{e}$ is the unit vector in the direction of the electric vector of luminous flux, and $\epsilon(\bar{\nu})$ is a function describing the form of the absorption band. Since the displacement of ground and excited levels in the field is much smaller

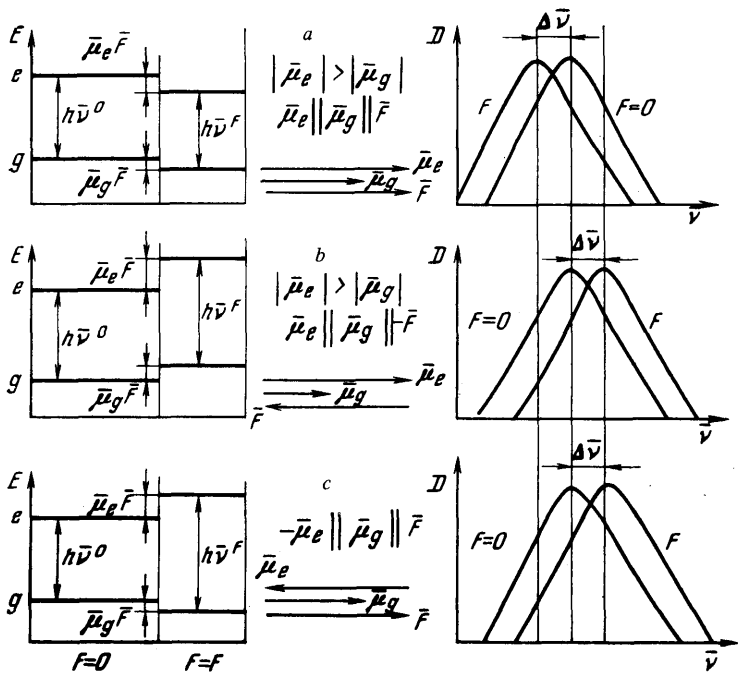


Figure 1. The effect of the mutual orientation of the vectors $\bar{\mu}_g$, $\bar{\mu}_e$, and $\bar{F}$ on the direction of displacement of the absorption band in the field: *a*) red shift; *b*), *c*) violet shift.

than the distance between them, the effect of the field can be estimated by a perturbation method:

$$\pi(\bar{\nu}^F) = \pi(\bar{\nu}^0) + \frac{d\pi(\bar{\nu}^0)}{d\bar{\nu}}\Delta\bar{\nu} + \frac{1}{2}\frac{d^2\pi(\bar{\nu}^0)}{d\bar{\nu}^2}\Delta\bar{\nu}^2 + \dots$$

Substituting for $\Delta\bar{\nu}$ from (1), we obtain

$$\pi(\bar{\nu}^F) = \pi(\bar{\nu}^0) + \frac{d\pi(\bar{\nu}^0)}{d\bar{\nu}}\left(\frac{\Delta\bar{\mu}\bar{F}}{hc} + \frac{\Delta\alpha\bar{F}^2}{2hc}\right) + \frac{1}{2}\frac{d^2\pi(\bar{\nu}^0)}{d\bar{\nu}^2}\left(\frac{\Delta\bar{\mu}\bar{F}}{hc} + \frac{\Delta\alpha\bar{F}^2}{2hc}\right)^2 + \dots \quad (2)$$

To determine the absorption of light by an ensemble of molecules it is necessary to add up the contributions by all molecules situated in the path of the light ray. Fig. 1 shows (*a* and *b*) that the spectral shifts of bands due to molecules whose dipole moments $\bar{\mu}_g$ are oriented along and against the field occur in opposite directions. As a consequence, only a slight broadening of the absorption bands, instead of a spectral shift to one side, is observed in a medium that is isotropic with respect to the directions of $\bar{\mu}_g$ and contains many molecules. This corresponds to the electrodynamic principle that effects which are linear with respect to the field cannot be observed in isotropic media. When the absorption of light by isotropic solutions is calculated, such linear effects are excluded because of the parity of the function of the cosine of the angle α between $\bar{\mu}_g$ and $\bar{F}$, and there remain only effects whose magnitude depends on $\bar{F}^2$. Effects proportional to higher powers of $\bar{F}$ can be neglected. Those proportional to $\bar{F}^2$ are termed *quadratic electrochromism*, in contrast to the linear electrochromism proportional to $\bar{F}$, whose nature will be examined in Section V.

In dilute solutions of polar molecules in a non-polar solvent an external field produces orientation polarisation, which Liptay[10] calculated from the Boltzmann distribution. In an electric field the medium becomes anisotropic, and effects that are linear with respect to the field become observable.

The final form of Liptay's equation is[11]

$$K = K_0 + A\frac{1}{\varepsilon(\bar{\nu})/\bar{\nu}}\frac{d(\varepsilon(\bar{\nu})/\bar{\nu})}{d\bar{\nu}} + B\frac{1}{\varepsilon(\bar{\nu})/\bar{\nu}}\frac{d^2(\varepsilon(\bar{\nu})/\bar{\nu})}{d\bar{\nu}^2}, \quad (3)$$

with the notation

$$K_0 = \frac{1}{10(kT)^2}\mu_g\frac{3\cos^2\gamma - 1}{2};$$

$$A = \frac{1}{5kThc}\left[\mu_g^2\frac{3\cos^2\gamma - 1}{2} - \mu_g\mu_e(\cos\gamma\cdot\cos\delta - \frac{1}{2}\sin\gamma\cdot\sin\delta)\right];$$

$$B = \frac{1}{10(hc)^2}\left[\mu_g^2\frac{3\cos^2\gamma - 1}{2} - 2\mu_g\mu_e(\cos\gamma\cdot\cos\delta - \frac{1}{2}\sin\gamma\cdot\sin\delta)\right] + \mu_e^2\frac{3\cos^2\delta - 1}{2};$$

$$K = -p_E\left[2{,}3D\left(\frac{\varepsilon_{DK}+2}{3}\right)^2\bar{F}^2\right]^{-1};$$

$\bar{\nu}$ (in cm^{-1}) the wave number, $\epsilon(\bar{\nu})$ the extinction coefficient, γ the angle between $\bar{m}$ and $\bar{\mu}_g$ with δ that between μ_e and $\bar{m}$, as before c the speed of light, ϵ_{DK} the dielectric constant of the medium, D the optical density, and p_E the measured degree of polarisation of light by the solution in the electric field. The field acting on the dissolved molecules had been calculated[10] by means of the Lorentz formula, but in later work Onsager's equation was used[12]. The theory of electrochromism and several of its applications have been discussed also in reviews[13-15].

Phenomena akin to electrochromism can be observed on application of an electric field to solutions whose components are in chemical equilibrium, provided that starting materials and final products differ in the sum of the products of the dipole moments of the ground state and the corresponding stoichiometric coefficients[16]. Electrochromism has been used to investigate charge-transfer complexes[17], conformational equilibria in which the components differ in polarity[18], and phenomena due to excitons[19].

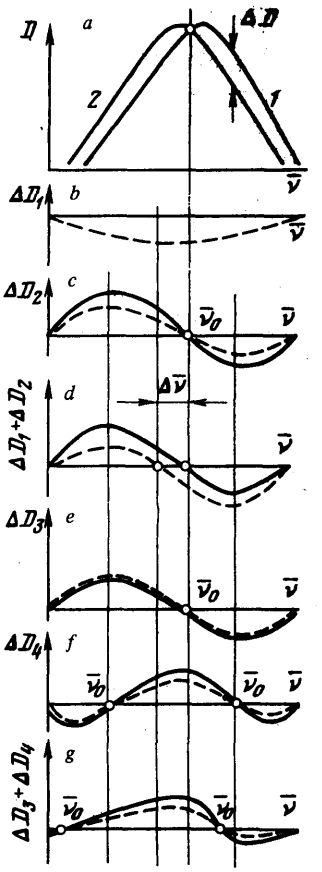


Figure 2. (*a*) Absorption spectra of solution: 1) in absence of a field; 2) under the influence of a field (the change in the spectrum has been greatly exaggerated for clarity). (*b*)–(*g*) Electrochromism spectra with $\theta = 55°$ and 90° (respectively full and broken curves), including (*b*)–(*d*) effects depending on orientation and (*e*)–(*g*) Stark effects: *b*) orientation effect ΔD_1 for molecule with $\gamma < 55°$ (when $\theta = 55°$ we have $\Delta D_1 = 0$, and the electrochromism spectrum coincides with the ordinate axis); *c*) orientation effect ΔD_2; *d*) spectral sum $\Delta D_1 + \Delta D_2$, with parameters of the electrochromism spectra $\Delta\bar{\nu}$ and $\Delta D_V/\Delta D_r$; *e*) quadratic Stark effect ΔD_3; *f*) linear Stark effect ΔD_4; *g*) spectral sum $\Delta D_3 + \Delta D_4$ (drawn with opposite sign to *f*).

Attention has been directed[2-4] to the dependence of the terms K_0 and

$$\frac{A}{\varepsilon(\bar{\nu})/\bar{\nu}}\frac{d(\varepsilon(\bar{\nu})/\bar{\nu})}{d\bar{\nu}}$$

in the Liptay equation (3) on the rotational mobility of the molecules. Quasi-stationary conditions are established in experiments on dilute solutions of polar molecules in a liquid non-polar solvent at external field frequencies far lower than those determining the movements of the solvent

molecules: dipole polarisation of the dissolved molecules is able to follow changes in the external field, and such molecules were termed "free". In other solvents or at other frequencies of the electric field "hindered" molecules may exist, for which the opposite frequency relation holds. Formula (3) characterises free molecules, whose orientation in the field obeys Boltzmann statistics. For hindered molecules the terms K_0 and A, containing the factor μ_g/kT, must be equated to zero.

Inspection of Eqns. (3) indicates that the electrochromism of free molecules has clearly defined features. The dependence of the electrochromism of polar probe molecules on the character of the molecular mobility of the test solvent forms the basis for application as a method of investigating molecular mobility in polymeric media. The Liptay equations were brought into line with the aims of the investigation by isolating as a separate group those effects of electrochromism that depend on the rotational mobility of the molecules (Fig. 2). The increase in optical density ΔD in the field, taken along the absorption band envelope, is measured as a function (termed the *overall electrochromism spectrum*) of the wavelength, frequency, or wave number (Fig. 2*a*):

$$\Delta D_{\theta=90^\circ} = (\Delta D_1 + \Delta D_2 + \Delta D_3 + \Delta D_4)_{\theta=90^\circ};$$

$$\Delta D_1 = \frac{1}{15}\left(\frac{\mu_g F}{kT}\right)^2 (1-3\cos^2\gamma)\, D;$$

$$\Delta D_2 = \frac{1}{5}\left(\frac{\mu_g F}{kT}\right)\frac{\Delta\bar{\mu}F}{hc}(2-\cos^2\gamma)\cdot\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}};$$

$$\Delta D_3 = \frac{1}{2}\frac{\Delta\alpha F^2}{hc}\cdot\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}; \qquad (4)$$

$$\Delta D_4 = \frac{1}{10}\frac{\Delta\bar{\mu}^2\bar{F}^2}{h^2c^2}(2-\cos^2\delta)\,\bar{\nu}\frac{\partial^2(D/\bar{\nu})}{\partial\bar{\nu}^2}.$$

These equations show that the overall spectrum is the sum of the contribution ΔD_1–ΔD_4, which are also electrochromism spectra, whose nature and dependence on molecular mobility and experimental conditions will be discussed below.

Equations (4) have been written for the case in which the relative directions of the electric vector of the light ray in the medium (unit vector $\bar{e}$) and the electric field $\bar{F}$ form the angle $\theta = 90^\circ$. We can vary the angle θ and select experimental conditions under which the contribution ΔD_1 can be eliminated from the overall electrochromism spectrum. The orientation effect ΔD_1 is due to orientation polarisation of the probe molecules and disregards Stark effects. It appears as Kuhn dichroism, for which[7]

$$\Delta D_{\theta=0^\circ} = -2\Delta D_{\theta=90^\circ}. \qquad (5)$$

For any angle θ we have

$$\Delta D_\theta = \Delta D_{\theta=0^\circ}\cdot\cos^2\theta + \Delta D_{\theta=90^\circ}\cdot\sin^2\theta. \qquad (6)$$

From (5) and (6) we find that

$$\Delta D_\theta = \Delta D_{\theta=90^\circ}(1-3\cos^2\theta).$$

The expression in brackets vanishes when $\theta = 54^\circ 44' \simeq 55^\circ$. Under these conditions $\Delta D_1 = 0$, and no orientation effect is observed (Fig. 2*b*). The probes usually chosen are molecules in which under conditions of symmetry the vectors $\bar{\mu}_g$, $\bar{\mu}_e$, and $\bar{m}$ are mutually parallel, while $\bar{\mu}_e > \bar{\mu}_g$ in absolute magnitude; we then have $\gamma = 0$ and $\delta = 0$, and for such molecules with $\theta = 55^\circ$ Eqns. (4) simplify to

$$\Delta D_{\theta=55^\circ} = (\Delta D_2 + \Delta D_3 + \Delta D_4)_{\theta=55^\circ};$$

$$\Delta D_2 = \frac{1}{3}\frac{\bar{\mu}_g\bar{F}}{kT}\frac{\Delta\bar{\mu}F}{hc}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}};$$

$$\Delta D_3 = \frac{1}{2}\frac{\Delta\alpha\bar{F}^2}{hc}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}; \qquad (7)$$

$$\Delta D_4 = \frac{1}{6}\frac{\Delta\bar{\mu}^2\bar{F}^2}{h^2c^2}\bar{\nu}\frac{\partial^2(D/\bar{\nu})}{\partial\bar{\nu}^2}.$$

Furthermore, an orientation effect is not observed under any conditions with molecules having the angle $\gamma = 55^\circ$, since the factor $1 - 3\cos^2\gamma = 0$ then vanishes (see formulae 4). Finally, an orientation effect is absent from media in which the rotational mobility of the probe molecules is hindered.

We have termed ΔD_2 (Fig. 2*c*) a *cross* electrochromism spectrum, since it results from two simultaneous effects of the field[3]. When the field is switched on, the original isotropic distribution of dipoles with respect to direction is disturbed, and anisotropy due to the factor $\bar{\mu}_g\bar{F}/kT$ appears. This permits observation of the Stark effect, linear with respect to the field and proportional to $\Delta\bar{\mu}\bar{F}$. As a consequence, the inherently linear Stark effect becomes proportional to $\bar{F}^2$. Obviously, no cross effect is observed in media with hindered mobility of the probes. When the angle θ changes from 90° to 55°, the cross effect diminishes by a factor $5/3 = 1.66$, as is evident from the coefficients in Eqns. (4) and (7).

Fig. 2*d* illustrates the spectral sum of the two contributions $\Delta D_1 + \Delta D_2$, which it is advisable to consider separately from the others, since only they depend on the rotational mobility of the molecules. The clearest indication of free rotation of the probes is a shift in the electrochromism zero point $\bar{\nu}_0$ with change in the angle θ from 90° to 55°. This is accompanied by a change in the ratio $\Delta D_V/\Delta D_R$ of the increases in the electrochromism signal on violet and red sides of the absorption band.

The contribution ΔD_3 (Fig. 2*e*) is made by the quadratic Stark effect, caused by the change in polarisability accompanying excitation of the molecule. The quadratic effect can be arbitrarily imagined to consist of two parts—an induced dipole moment $\Delta\alpha\bar{F}$ and a linear Stark effect—the former always lies in the direction of the field irrespective of the rotational mobility of the molecules, and the latter depends on the interaction of the induced moment with the same external field $(\Delta\alpha\bar{F})\bar{F}$. With $\alpha_e > \alpha_g$ this leads to a red shift of the band.

For every moment $\Delta\bar{\mu}$ in an isotropic medium containing a large number of molecules it is always possible to find another molecule having the same moment but oriented in the opposite direction. If one orientation corresponds to a red shift of the absorption band in the field as a consequence of a first-order Stark effect, the opposite orientation corresponds to a violet shift. Only a slight broadening of the band can then be observed, proportional to $\partial^2(D/\bar{\nu})/\partial\bar{\nu}^2$. We have termed the ΔD_4 effect *linear* in conformity with its nature (Fig. 2*f*), although it is found to be proportional to $\bar{F}^2$. It does not depend on rotational mobility, so that a sensible procedure is to combine it with ΔD_3 and henceforward consider another spectral sum $\Delta D_3 + \Delta D_4$ (Fig. 2*g*). A characteristic feature of $\Delta D_3 + \Delta D_4$ spectra in media with free rotational mobility of probe molecules whose dipole moments $\bar{\mu}_g$ and $\Delta\bar{\mu}$ are a few Debyes is their low intensity in comparison with $\Delta D_1 + \Delta D_2$ (Fig. 2*d*). In this case effects depending on orientation exceed Stark effects by factors of $\sim 10^{1.5}$. In media with hindered rotation of probe molecules, on the other hand, only Stark effects can be observed with two zero points $\bar{\nu}_0$, whose positions are independent of the angle θ.

Thus, if the originally free rotation of molecules is gradually hindered, e.g. by freezing the solvent, the electrochromism spectra change from the spectral sum $\Delta D_1 + \Delta D_2 + \Delta D_3 + \Delta D_4$ to the spectrum $\Delta D_3 + \Delta D_4$ with a corresponding decrease in intensity by factors of $10^{1-1.5}$.

Inspection of Eqns. (4) and (7) shows that orientation-dependent effects diminish at different rates with rise in temperature: the orientation effect falls more rapidly. With rise in temperature to infinity both orientation and cross effects tend to zero.

For the study of slow movements in macromolecules it is very important to examine the frequency dependence of individual effects. Only molecules whose rotational relaxation time is shorter than the period of the alternating field $\bar{F}$ reveal $\Delta D_1 + \Delta D_2$ effects. Thus probe molecules are arbitrarily divided into two groups—free and hindered—by the frequency of the external field. In very high-frequency fields all molecules may be hindered, and at very low frequencies all can be regarded at least hypothetically as free. These considerations show that, by examining electrochromism spectra over a wide range of field frequencies, information can be obtained on the spectrum of relaxation times of probes in polymers. Frequency begins to influence Stark effects only in the range in which relaxation processes are appreciable in the electron shells of the molecules[20]. As a consequence, under normal conditions Stark effects make a constant contribution and provide a kind of standard, with which effects depending on orientational mobility can be compared.

Thus the concept of overall electrochromism spectra as a sum of contributions, together with specific observed features, underlies a technique for their separate determination, which is based on the following principles[2].

1. Cross and orientation effects are not observed in media with completely hindered rotational mobility. In this case the form and the intensity of the electrochromism spectra are determined by Stark effects. Parameters of the electrochromism spectra due to the latter effects, which are characteristic of media with hindered mobility, are maintained in media with free motion of the same molecules.
2. No orientation effect is observed when the polarisation of the light ray corresponds to $\theta = 55°$.
3. The cross effect and the quadratic Stark effect are zero at the peak of the absorption band, where $\partial (D/\bar{\nu})/\partial \bar{\nu} = 0$.
4. The linear Stark effect is zero at points at which $\partial^2(D/\bar{\nu})/\partial \bar{\nu}^2 = 0$.
5. For molecules having $\gamma = 0°$ the cross and linear effects increase by factors of 1.66 as the angle θ diminishes from 90° to 55°.

III. INVESTIGATION OF AMORPHOUS POLYMERS IN VITREOUS-ELASTIC TRANSITION RANGE BY QUADRATIC ELECTROCHROMISM

Electrochromism effects can be determined separately in a polymer matrix at a temperature in the region of transition from elastic to vitreous states. Fig. 3*a* illustrates the absorption spectrum (curve *1*) and the electrochromism spectra of *p*-dimethylamino-*p'*-nitrobisazobenzene in polystyrene at room temperature (below the glass point). It is evident that the electrochromism spectra for $\theta = 55°$ and 90° differ merely in intensity, with

$$\Delta D_{\theta=55°}/\Delta D_{\theta=90°} = 1.66.$$

It follows from theory that these spectra correspond to complete hindrance of probe molecules in the polystyrene. This is supported also by the presence of two electrochromism zero points, whose positions are independent of the angle θ, as well as by the similarity of the spectra to those illustrated in Fig. 2*g*. The ΔD_3 and ΔD_4 effects can be separated by means of the difference in shape between the corresponding electrochromism spectra. The ΔD_3 spectrum is proportional to the first derivative of optical density with respect to frequency, so that at the peak of the band $\Delta D_3 = 0$: the ordinate of the $\Delta D_3 + \Delta D_4$ electrochromism spectra at this wavelength gives only the ΔD_4 contribution (see Fig. 2*f*). With the second derivative $\partial^2(D/\bar{\nu})/\partial \bar{\nu}^2$ available we can normalise its value at the band maximum and then calculate the ΔD_4 contribution throughout the spectrum. The ΔD_3 contribution is found similarly from the vanishing of ΔD_4 at zero points of the second derivative, when the effects are determined solely by the ΔD_3 signals. Another possible method is based on the additivity of the optical densities: ordinates of the ΔD_4 contribution calculated throughout the spectrum can be subtracted from the $\Delta D_3 + \Delta D_4$ spectrum. The electrochromism spectra should be taken at corresponding angles θ.

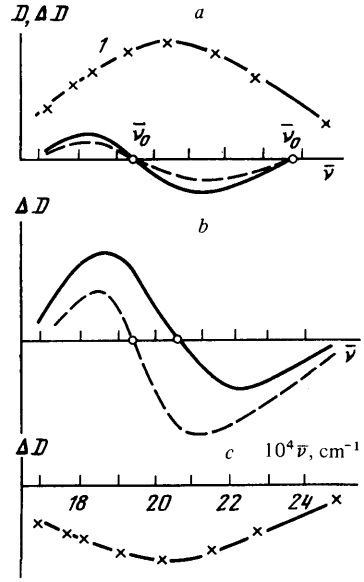


Figure 3. (*a*) Electrochromism spectra of (III) (Fig. 5) in polystyrene at room temperature: -----) $\theta = 55°$; - - -) $\theta = 90°$; 1) absorption spectrum; ×) form of contribution by orientation effect coinciding with absorption band. (*b*) Electrochromism spectra of the same specimen above the glass point. (*c*) Calculation of orientation effect.

When a specimen is heated the electrochromism spectra gradually change in the transition range (75–90°C). Fig. 3*b* shows overall electrochromism spectra for the same specimen heated to 92°C, i.e. above the glass point. Comparison with Fig. 2*d* reveals that these spectra correspond to orientational mobility of the probes. The spectra contain a single zero point, whose position depends on the angle θ: when $\theta = 55°$, the zero point is close to the peak

of the band. The slight displacement from the band maximum is attributed to a contribution by Stark effects. To determine the ΔD_1 and ΔD_2 contribution it is necessary to subtract the Stark effects obtained for the vitreous state from the overall electrochromism spectra at corresponding angles θ. After such subtraction the electrochromism spectrum at $\theta = 55°$ corresponds to the cross effect ΔD_2 with its zero point at the peak of the band. Determination of ΔD_1 requires subtraction from the electrochromism spectra at $\theta = 90°$ of $\Delta D\theta = 55°/1.66$, since the cross effect decreases by the factor 1.66 when the angle θ changes from 55° to 90° (Fig. 2*c*).

As a check we must compare the ΔD_2 contribution with the form of the first derivative of optical density with respect to frequency, and ΔD_1 with the form of the absorption band (bearing in mind that the ΔD_1 effect is negative for molecules having $\gamma < 55°$). The agreement between ΔD_1 (Fig. 3*c*) and the absorption band is shown by the points (×) on Fig. 3*a*.[21] The calculations were based on the hypothesis that the reaction field remains unchanged when specimens are heated above the glass point from room temperature. This hypothesis holds quite well for polystyrene, whose dielectric constant is only slightly dependent on temperature. With other polymers, e.g. poly(vinyl acetate), the dielectric constant increases rapidly with temperature, so that spectra obtained at different temperatures must be corrected for the reaction field when they are subtracted or added.

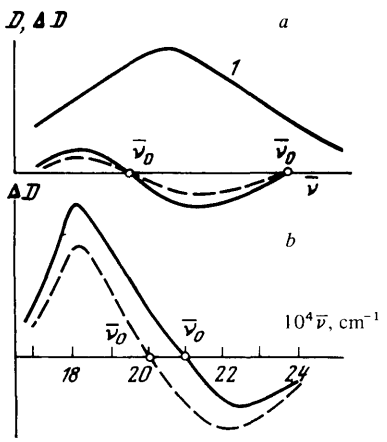


Figure 4. Effect of solvent (benzene) residues on electrochromism spectra of (II) (Fig. 5) in polystyrene specimen with different angles θ: -----) 90°; - - -) 55° at different temperatures: *a*) 20°C (specimens dried in air at room temperature for 24 h, and then in a vacuum at 60°C); 1) absorption spectrum; *b*) 95°C (dried only in air for 24 h).

A spectrophotometer is used to obtain the absorption spectrum, but the derivatives $\partial(D/\nu)/\partial\bar{\nu}$ and $\partial^2(D/\bar{\nu})/\partial\bar{\nu}^2$ are calculated from the spectrum, either by using a Gaussian function to approximate to the absorption band or by numerical differentiation on an electronic computer. Probe molecules are introduced into polymers by mixing separately prepared solutions of polymer and dye in a suitable solvent. The solvent is then removed initially by evaporation and then by drying the coloured polymer mass (Section VI). Benzene is a solvent for polystyrene, and therefore exerts a plasticising action on the latter; the benzene remaining in the specimen after drying affects the mobility of the probes. Specimens having different benzene contents can be obtained by varying the drying conditions.

Fig. 4*a* illustrates the electrochromism spectra of an azo-dye in polystyrene at room temperature for a specimen from which benzene has been completely removed by drying. Molecular mobility in the specimen is hindered, as indicated by the form of the electrochromism spectra and the unchanged position of the $\bar{\nu}_0$ points when the angle θ is varied. Fig. 4*b* gives electrochromism spectra for a specimen from which removal of solvent is incomplete as a consequence of milder drying conditions. The difference in mechanical properties between the two specimens is slight, with the former slightly more brittle. Yet the mobilities of probes in them differ substantially. The electrochromism spectrum (Fig. 4*b*) has clearly defined features indicating rotational mobility of the probes in polystyrene[2].

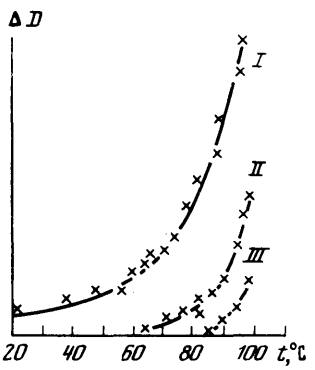
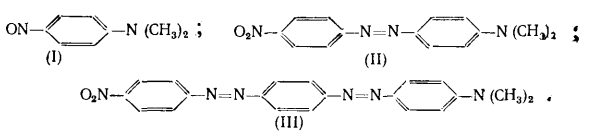


Figure 5. Temperature dependence of orientation effect in polystyrene film for the three probe molecules differing in size



The electrochromism spectra depend on the size of the probes (Fig. 5). The smallest probes—nitrosodimethylaniline (I) molecules—possess appreciable rotational mobility at a frequency of 240 Hz in polystyrene even at room temperature. *p*-Dimethylamino-*p'*-nitroazobenzene(II) molecules are able to rotate at 64°C, but the largest probes—*p'*-dimethylamino-*p*-nitrobisazobenzene(III) molecules containing three benzene rings—begin to rotate at 85°C. The results are well explained by the theory of the dynamic free volume[22].

IV. STUDY OF ELASTIC STATE OF AMORPHOUS POLYMERS BY QUADRATIC ELECTROCHROMISM

Fig. 6 illustrates absorption and electrochromism spectra of probe (II) obtained under the same conditions in certain rubbers. The form and the intensity of the electrochromism spectra obviously depend on the type of polymer. The ratio of the contributions made by two groups of effects—(i) $\Delta D_1 + \Delta D_2$, depending on the rotational mobility of the probes, and (ii) Stark effects, which are the same in all specimens—is found to determine the whole variety of spectral forms. Differences in intensity depend also on the strength of the field acting on the molecules with the same external electric field. In the investigation of molecular mobility the reaction field for media of dielectric constant ~2 can be calculated[2-4] by means of the Lorentz formula. In media of high dielectric constant (in SKN-26 and Nairit rubbers), however, this formula is inapplicable. Fröhlich calculation[12] of the field shows that the reaction field in SKN-26 of dielectric constant 11 is one-third of the Lorentz field, which diminishes the densities of field-quadratic effects by ~90%. In order to estimate rotational mobility in such cases it is advisable to compare the parameters $\Delta D_V/\Delta D_R$ and $\Delta\bar{\nu}$, which determine only the form of the spectrum (Fig. 2). It follows from these that rotational mobility of probe (II) in SKN-26 and Nairit rubbers does not greatly differ from that of the same probe in other rubbers.

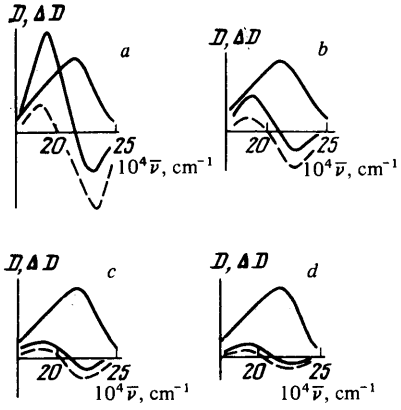


Figure 6. Absorption and electrochromism spectra of (II) at room temperature in various rubbers: *a*) SKS-30 [styrene-butadiene]; *b*) SKS-30-1; *c*) SKN-26 [butadiene-nitrile]; *d*) Nairit [chloroprene].

A very interesting question is the mechanism of the motion of probe molecules in a polymer. According to one view the polymer is a continuous, structureless medium, characterised by a single parameter—its viscosity—and thus having one rotational relaxation time of probes†. A second view assumes a broad spectrum of relaxation times[23], in which the same molecule is able to change sharply its relaxation characteristics, passing abruptly from free to hindered states and back. The two views lead to the same electrochromism spectra, so that additional information is required to make a choice between them‡. For this purpose our experiments[2] included examination of the phase shift between electrochromism signal and external field. In the former case, with viscous flow of the probes, the phase shift should differ from zero, since the proportions of free molecules $1 > \sigma > 0$ (Table 1) would appear to indicate that electrochromism measurements are made in a region of dispersion of rotational mobility of the probe. In the latter case, with a broad spectrum of rotation relaxation times of the probes, the phase shift should be zero, as was observed in all the rubbers investigated. The experiments with polystyrene (Figs. 3 and 4) and poly(methyl methacrylate) show that the rotational mobility of the probes changes significantly in the region of vitrification. It might have been expected that a phase shift would have been detected between the electrochromism signals and the external field with slow variation in temperature over the transition range. However, even in these experiments the phase shift was zero. It must thus be supposed that macromolecules in amorphous linear polymers have a broad spectrum of relaxation times. In terms of the theory of free volume[22] this implies that the probe is free at those instants in which a free volume—a cavity large enough to permit rotation of the probe—is formed around the probe as a consequence of the thermal motion of the macromolecules. In the next instant the cavity "collapses", and the probe passes into the hindered category.

Table 1.

Polymer	σ	$10^{-16}a$	$10^{-5}k_{tr}$, min^{-1}
SKS-30-1	0.22	74	3.4
Polyethylene	0.26	93.5	350
Natural rubber	0.40	137	250
SKMBP-5	0.44	153	2.9
SKB [butadiene rubber]	0.44	153	16.5
SKS-30	0.49	180	8.0

Interpretation of the electrochromism spectra as the summation of contributions by Stark effects and effects depending on orientational mobility enables the proportion of free molecules to be found. This requires comparison of $\Delta D_1 + \Delta D_2$ electrochromism spectra obtained under the same conditions in the test medium and in a liquid solvent of low molecular weight and closely similar dielectric constant, in which rotational mobility has characteristic times of 10^{-10}–10^{-12} s and all probes can be regarded as free. Instead of determining the spectra in the liquid we can use formulae (4) and (7) to calculate $\Delta D_1 + \Delta D_2$ for probes whose parameters have already been measured. Table 1 lists proportions σ of free (II) molecules at 240 Hz in various rubbers at room temperature. It includes the

† Actually, three relaxation times are possible for non-spherical molecules, corresponding to rotation about the three principal axes, but this does not affect the generality of the argument.

‡ Criteria for establishing whether the motion of molecules in liquids occurs by diffusion or in jumps were defined in Ref. 24.

corresponding orientation coefficients $a = \Delta D_1/DF^2$, which contain the contribution ΔD_1 isolated from the overall electrochromism spectrum by the method described above. The proportion of free molecules σ was obtained by comparing the intensities of the electrochromism spectra of the probe (II) in the rubbers and in benzene. It may be supposed *a priori* that the ratio a/σ of the values in Table 1 should be constant for all the rubbers: in fact, the relative variation in the ratio is ~3%, which supports the general physical significance of a and σ.

It was of interest to establish the relation between rotational and translational diffusion of probe molecules in polymeric media. A method was therefore devised for studying translational diffusion by measuring rates of crystallisation of the probes from polymeric media[25]. Table 1 gives true crystallisation rate constants k_{tr}, which characterise the translational mobility and must be compared with the orientational coefficients or the proportions of free molecules σ. The comparison reveals no correlation between parameters characterising slow rotational and translational diffusion for the probe (II) in the rubbers at room temperature.

V. INVESTIGATION OF VITREOUS STATE OF AMORPHOUS POLYMERS BY LINEAR ELECTROCHROMISM

When a specimen is subjected to the simultaneous action of two electric fields—an alternating field $\bar{F}\sin\omega t$ and a constant field $\bar{F}_0$—the resultant field $\bar{F}\sin\omega t + \bar{F}_0$ produces in quadratic electrochromism effects proportional to

$$\bar{F}^2\sin^2\omega t + 2\bar{F}\bar{F}_0\sin\omega t + \bar{F}_0^2 = -1/2\bar{F}^2\cos 2\omega t + 1/2\bar{F}^2 + 2\bar{F}\bar{F}_0\sin\omega t + \bar{F}_0^2.$$

The first term defines the quadratic electrochromism considered above; it is observed in the frequency channel 2ω, i.e. at double the frequency of the electric field. The second and fourth terms are responsible for effects independent of the frequency of the field, which can be detected in the channel $\omega = 0$. The third term represents effects that are linear with respect to the alternating field, which are recorded in the frequency channel ω, i.e. at the frequency of the field. Thus the combined action of two fields produces electrochromism effects that are recorded in different frequency channels and have several specific features. By superposing the fields $\bar{F}\sin\omega t + \bar{F}_0$ we can investigate all the electrochromism effects discussed already—Eqns. (4) and (7)—but examination of the ΔD_2 effect is of especial interest for determining molecular mobility. This effect has a dual nature (Fig. 2*c*): one component factor $\Delta\bar{\mu}\bar{F}$ is due to the linear Stark effect, and the other $\bar{\mu}_g\bar{F}/kT$ to the degree of anisotropy in the directions of dipole moments resulting from the action of the same electric field $\bar{F}$. Anisotropy can in principle be produced by the additional independent constant field $\bar{F}_0$. The formula for the effect that is linear with respect to the field can then be written for $\theta = 55°$ in the form

$$\Delta D_2^l = \frac{1}{3}\frac{\bar{\mu}_g\bar{F}_0}{kT}\frac{\Delta\bar{\mu}\bar{F}}{hc}\bar{\nu}\frac{\partial(D/\bar{\nu})}{\partial\bar{\nu}}. \qquad (8)$$

Elongated probe molecules having $\bar{\mu}_g$ and $\Delta\bar{\mu}$ of a few Debyes and the angles $\gamma = 0$ and $\delta = 0$ are usually chosen for the investigation of molecular mobility. With $\theta = 55°$ the orientation effect ΔD_1^l is not observed, while ΔD_3^l and ΔD_4^l are small in comparison with ΔD_2^l. The ΔD_2^l effect therefore predominates, and the contributions by other effects can be neglected. It has been suggested[2,3,26] that linear electrochromism can be used to investigate very slow relaxation processes in vitreous polymers. For this purpose a procedure was devised in which a polymer specimen into which probes had been introduced was heated above the glass point and placed in an alternating field $\bar{F}$. Only quadratic electrochromism at frequency 2ω can then be observed: no linear effect is observed at the frequency of the field $\bar{F}$. If at the same time a constant field $\bar{F}_0 = 10^3$–10^4 V cm^{-1} is applied to the specimen, anisotropy appears in the directional distribution of dipoles $\bar{\mu}_g$, observation of the linear effect for molecules oriented by the constant field becomes possible, and a linear electrochromism signal is produced.

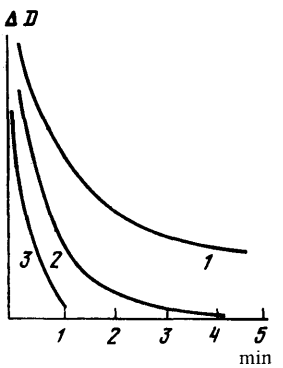


Figure 7. Kinetic curves for the decay of the linear electrochromism signal of (II) in polystyrene at (°C): 1) 78; 2) 85; 3) 99.

The specimen can then be cooled below the glass point (to the experimental temperature) without removal of the constant field $\bar{F}_0$; this freezes the rotational mobility, after which the constant field is removed. At the instant at which the field $\bar{F}_0$ is switched off the anisotropy begins to disappear at a rate depending on the molecular mobility in the medium at the experimental temperature; at the same time the linear electrochromism signal becomes weaker. In liquid solvents of low molecular weight this signal disappears almost instantaneously when the constant field is switched off. In polymeric plastics with sufficiently dense packing at temperatures below the glass point it remains for a long time[2]. The variation in the linear electrochromism signal with time gives a kinetic curve characterising the dynamics of molecular movements in the medium (Fig. 7).[26] One of the most interesting experimental results is the discrete spectrum of relaxation times of molecular motions in vitreous polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) with substantially different characteristic times. The corresponding processes can easily be separated by a simple method based on isolating the straight segment in the terminal regions of the kinetic curves plotted in the semi-logarithmic coordinates $\ln\Delta D$ against time on the assumption that all the relaxation processes forming the spectrum begin simultaneously at the instant the field $\bar{F}_0$ is switched off. The first component $\Delta D'$ isolated in this way, with the longest relaxation time τ', is subtracted from the overall spectrum, and the procedure is repeated for the difference $\ln(\Delta D - \Delta D')$; and so on, until the whole kinetic curve has been exhausted[27].

To estimate the lower frequency limit to the determination of relaxation times by means of linear electrochromism we assume the possibility that a specimen can exist with an infinitely long relaxation time, in which the anisotropy of the directional distribution of dipole moments of probes always remains the same. Theory shows that this case corresponds to a linear electrochromism signal that remains unchanged with time. It is evident from this example that the method has no lower frequency limit. A polystyrene specimen containing the probe (III) exhibited a linear electrochromism signal at room temperature for a month, after which observation was discontinued[2]. Calculation showed that the decay process corresponded to a mean relaxation time of about 2 weeks or 10^6 s. The most rapid processes that can be observed with our apparatus (see below) have relaxation times of a few seconds (this limit is determined by the time constant of the recording instrument). Table 2 gives relaxation times τ for three exponential processes isolated from the kinetic curves, together with their contributions δ, at various temperatures. These data can be used to calculate energies corresponding to the two slowest processes, by means of the equation

$$\tau = \tau_0 \exp(-\Delta E/kT),$$

which gives for ΔE_1 and ΔE_2 the respective values 1.87 and 0.78 eV. These quantities are difficult to interpret, since information on the mechanisms of relaxation processes in vitreous media is extremely limited. From Table 2 it can be concluded that the structure of the spectrum of relaxation times changes with rise in temperature, in such a way that the contribution by rapid relaxation processes increases, while that by slow processes diminishes. Analogous changes in spectra of relaxation times are observed in the plasticisation of specimens[2].

Table 2. Relaxation times τ (s) and contributions δ of rotational motions of *p*-dimethylamino-*p'*-nitrostilbene in polystyrene at various temperatures, isolated from the relaxation-time spectrum.

t, °C	τ_1	δ_1	τ_2	δ_2	τ_3	δ_3
71	4800	0.18	445	0.23	160	0.08
78	1620	0.145	160	0.23	30	0.15
84.5	525	0.11	45	0.20	—	—
88.5	240	0.12	24	0.18	—	—
90	188	0.095	20	0.11	—	—
92.5	40	0.10	—	—	—	—
94	15	0.09	—	—	—	—

VI. EXPERIMENTAL PROCEDURE

The electrochromism of molecules having large dipole moments in ground and excited states can be detected with a mass-produced spectrophotometer designed for chemical analysis using electric fields of limiting permissible strength $\sim 10^6$ V cm^{-1}.[28] This method is completely unsuitable for recording electrochromism spectra in the most common cases, in which the signals do not exceed 10^{-4}–10^{-5} unit of optical density. Several types of equipment have been described for special purposes, mainly for investigating excited states of molecules[29]. An idea of the simplest apparatus for recording electrochromism spectra in the investigation of molecular mobility in polymers can be found in a previous paper[30]; an improved form will be described below, together with the procedure.

1. Preparation of Specimens

Probes are introduced into linear polymers—plastics and rubbers—by dissolving the latter in a suitable solvent, e.g. benzene, and mixing the resulting solution with a solution of the probe dye in the same solvent[28]. The relative volumes of the solutions are so chosen that specimens having a dye content of 10^{-3}–10^{-4} mole per 1000 g polymer are obtained after the solvent has vaporised. Firstly the solvent evaporates from a Petri dish at room temperature, and then the coloured film is dried in a vacuum drying vessel at 50–60°C for 24 h. Under these conditions benzene is completely removed from the polymer, as can be checked from the electrochromism spectra (Fig. 4). Films having plane-parallel surfaces are formed by placing the coloured mass between small sheets of pure transparent mica free from cracks, air bubbles, or foreign inclusions. The sheets are separated by gaskets 100 μm thick located along the edges of the sheets, and are compressed in a press heated to 100–110°C. On softening, the polymer fills the space between the mica sheets and bonds to them firmly. The mica prevents the films from buckling and determines the breakdown voltage of the specimen. The coloured film together with the mica sheets is glued by means of an epoxy-resin between transparent ground-glass electrodes 20 × 20 mm in size. A conducting coating is obtained by depositing tin dichloride vapour on the glass surfaces heated to 400–420°C.[31]

2. Apparatus for Recording Electrochromism Spectra

The probe molecules chosen for studying molecular mobility in polymers are dyes, whose absorption spectra are located in the visible spectrum. Therefore an overrun lamp *1* (Fig. 8) was used as source, the luminous flux from which was stabilised by using a device *2* to stabilise the current. The polychromatic light from the lamp is directed to the inlet slit of a monochromator *3*, the ray first passing through a light modulator *4*, which is necessary to record the action spectra of the apparatus (the modulator is disconnected for the determination of electrochromism spectra). The monochromatic light passes through an inclined quartz plate to balance the inherent polarisation of the monochromator (not shown in Fig. 8), and then falls on the Polaroid film *5*. The polarised monochromatic light is directed on the specimen *6* placed in a thermostat *7* filled with mineral oil as heat-transfer agent. The temperature of the specimen can be varied from 20 to 150°C and maintained constant to 0.5 deg by means of a thermostatic unit *8* connected to an electric heater immersed in the thermostat and provided with a resistance thermometer. The light ray emerging from the specimen, modulated to an extent of 10^{-4}–10^{-5}, falls on a photocell *9* placed in a detachable photometric head *10*. The electric signal is fed to the input of the low-frequency amplifier *11*, which has an amplification band of 420 Hz with band-width 0.8 Hz and amplification factor 12000. The amplified signal reaches the phase-sensitive detector *12* and the oscillograph *13*; the latter is designed

to record the most intense electrochromism signals, but is used mainly to observe the noise in the apparatus. From the phase-sensitive detector the signal enters an *RC* circuit (not shown in the diagram), which determines the time constant of the system, and then the input of a direct-current amplifier *14* followed by the pen-recorder *15*. The motion of the chart of *17* is synchronised with the spectrum-scanning device *16*.

An alternating voltage of frequency 210 Hz is fed from an oscillator *18* through a step-up transformer *19* to the specimen. By controlling the output of the oscillator the voltage on the specimen can be varied over the range 0–2 kV. Linear electrochromism effects are observed at the field frequency ω, but quadratic effects at the doubled frequency 2ω. In order to be able to use in both cases the same amplifier tuned to the frequency 420 Hz, the field frequency was set at 210 Hz for the investigation of quadratic effects. As a consequence, measurement of such effects required that the frequency of the reference signal should also be doubled, which was achieved by means of the unit *20*. In the investigation of linear effects the frequency doubler *20* was disconnected. The signal of the reference voltage is fed through the phase shifter *21* to the phase-sensitive detector *12*. In the investigation of linear electrochromism a constant voltage from a high-voltage source *22* is superimposed on the alternating field on the specimen.

The field-modulated luminous flux is

$$I_F = I_0 T T' T_F,$$

where I_0 is the luminous flux incident on the specimen, T the transmission of light by the specimen, T' the light losses due to the cuvette, and T_F the transmission of light by the specimen that is due to the action of the field $\vec{F}$. Expanding T_F as a series and retaining only the first two terms in view of the smallness of $\Delta D'$, we obtain

$$T_F = e^{-\Delta D'} = 1 - \frac{\Delta D'}{1!} + \frac{\Delta D'^2}{2!} - \ldots;$$

on passing to a decadic base, we find that

$$I_F = I_0 T T' - 2{,}3 I_0 T T' \Delta D.$$

The first term is a constant component of the luminous flux, which is not recorded by the instrument. The second term includes the alternating unknown quantity ΔD, whose variation with wavelength gives the electrochromism spectrum.

The luminous flux I_0 depends on the action spectrum of the apparatus, which must be corrected for. However, it is more expedient to correct not the incident but the transmitted luminous flux, thereby allowing for the transmission both of the specimen and of the cuvette. Two methods are employed for this purpose[26].

1. In order to correct the form of the electrochromism spectra the luminous flux of the instrument with the specimen fitted in it is modulated by means of a light chopper with the electric field switched off. The signals from the chopper are recorded on the pen-recorder chart as a function of wavelength. This involves switching the unit *12* from a phase-sensitive to an amplitude detector. A particular wavelength is then selected within the electrochromism spectrum, the chopped signal at which is taken to be unity, and signals obtained at other wavelengths are normalised to this value. The true form of the electrochromism spectrum is obtained by dividing its ordinates by the normalised values of the chopped signals at corresponding wavelengths. Such plots can be used in most cases in investigating molecular mobility on specimens for which the relative intensities of the electrochromism spectra are quite high. Absolute increases in optical density can be found by comparing the electrochromism spectrum of the test substance with that of a standard substance recorded under the same conditions. *p*-Dimethylamino-*p'*-nitrostilbene, for whose molecules the parameters of ground and excited states are well known, has been used as standard in our work.

2. The electrochromism spectrum is drawn through points obtained at 10–15 selected wavelengths. The specimen is placed in the instrument, and the light chopper is switched on with the field switched off. For all these wavelengths monochromator slit widths are then selected to correspond to signals having the same amplitude. The slit openings thus found are then used in determining the electrochromism spectrum, which will give directly ordinates of the corrected spectrum. Absolute values of the signals are found, as in the first method, by comparison with the electrochromism spectrum of a standard substance.

3. Measurement of the Angle θ

The specimen is fixed in the thermostatted cuvette at an angle to the luminous flux (Fig. 9) such that the angle between the surface of the specimen and the direction of

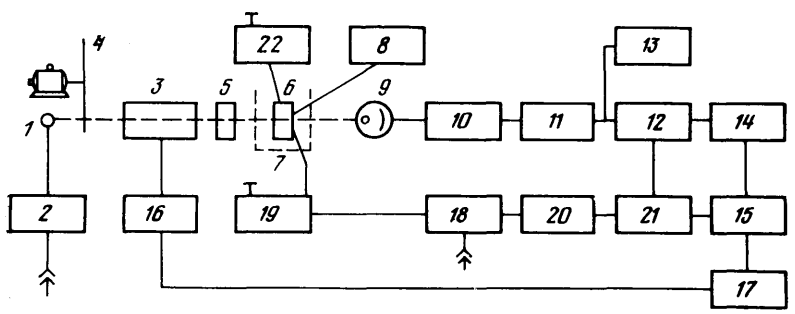


Figure 8. Block diagram of apparatus for recording electrochromism spectra (key in text).

the ray in the test medium is 54°44′ ≈ 55°. With the light polarised in a vertical plane the angle between the vectors $\bar{e}$ and $\bar{F}$ is then $\theta = 90°$, but with horizontal polarisation this becomes 55°.

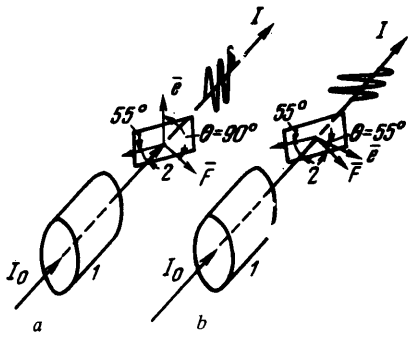


Figure 9. Diagram illustrating the variation of the angle θ as the Polaroid is rotated: 1) Polaroid; 2) specimen; $\bar{e}$) unit vector in direction of electric vector of light wave; I_0), I) luminous fluxes; *a*) vertically polarised light; *b*) horizontally polarised light.

The direction of light in the medium depends on the ratio of the refractive indices of the medium and of the oil filling the thermostat. If the refractive indices differ greatly, the angle at which the specimen is fitted must be corrected.

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The above survey shows that the study of electrochromism will yield important information on movements in polymer molecules. The method can be developed firstly to investigate proper motions of fragments of macromolecules containing chromophores absorbing in the visible and ultraviolet, when the need for interpretation of indirect results obtained by the probe method is eliminated. A second development would be to record spectra of relaxation times of molecular movements, which can be obtained with wide variation in the frequency of the electric field and by means of the quadratic electrochromism spectrum or by analysis of kinetic curves from linear electrochromism spectra. The value of relaxation-time spectra lies in their relationship both to the motion of definite groups of atoms and to the thermodynamic properties of the medium, i.e. the properties of polymeric materials.

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Photochemical Methods for Recording Information. Primary Photoprocesses

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The principal photographic characteristics of non-silver materials, whose activity is based on photochemical reactions, are presented. The nature of the first stage in the photochemical processes involving the recording of information (the primary photochemical reaction) are analysed and the kinetic approach to the estimation of some of their limiting characteristics is discussed. Materials are classified in terms of the primary photochemical reactions and the threshold of the energetic light sensitivity and the red limit of the region of spectral sensitivity are estimated for each primary reaction.
The bibliography includes 163 references.

CONTENTS

I.	Introduction	317
II.	Photographic characteristics of non-silver materials whose activity is based on photochemical reactions	319
III.	General scheme for the kinetic analysis of the photochemical stage in the recording of information. Principal approximations.	319
IV.	Classification of light-sensitive materials in terms of primary photochemical reactions	321
V.	Relation between the red limit of the spectral sensitivity of materials and the kinetic and spectroscopic constants of light-sensitive substances	321
VI.	Conclusion	328

I. INTRODUCTION

Among the problems of modern photographic science, the following occupy a central position: the search for highly effective light sensitive materials, the prediction of their properties, and estimation of the limiting values of the principal characteristics of such materials. The properties of individual non-silver chemical materials and processes have been examined in reviews devoted to specific photographic materials: photochromic materials[1-21], materials with physical development[22-30], light-sensitive polymers[31-34], photopolymerisation materials[34-43], diazotype materials[44-52], vesicular materials[52-55], and free-radical materials[56-63]; they are also considered in general reviews[64-78].

In order to solve the problems indicated above, it is necessary to establish a relation between the photographic characteristics of light-sensitive materials and the physicochemical properties of the initial light-sensitive substances.

We shall consider a general approach to the solution of this problem. Fig. 1 presents a scheme for the production of an image when chemical non-silver photographic processes are used. Evidently the production of an

image with the aid of these materials involves several stages. Stage (1) is a photochemical reaction with formation of the primary photoproduct. In individual instances (pathway *A*) the primary product already constitutes a centre for the formation of the image. However, as a rule (pathway *C*) the primary product initiates in stage (2) further dark reactions with formation of a latent image. As a result of stage (3), the latent image is developed (or intensified) and centres of the final image are produced. Sometimes (pathway *B*) the primary photoproduct constitutes the latent image and in this case there is no second stage in the production of the image. The properties of the resulting image are determined by all three stages, so that the determination of a relation between the photographic characteristics of light-sensitive materials and the physicochemical properties of the initial sensitive system is a complex problem and involves the analysis of each stage.

It is in general impossible to carry out a complete analysis of the entire set of processes. This review is devoted to the analysis of the first stage of the production of the image—the primary photochemical reaction. On the basis of this analysis, certain limiting parameters of photographic materials are estimated. The second and third stages in the production of the image (dark reactions and intensification processes) as well as sensitisation problems are not discussed.

If the image formation process has only one stage (pathway *A*, Fig. 1), then the estimates yield the limiting characteristics in the materials. In the presence of other stages (cases *B* and *C*) the estimates constitute the lower limits of the values of these characteristics.

The group of non-silver photographic processes for the recording of information is very large and includes photochemical reactions in non-silver light-sensitive materials based on organic and inorganic compounds, photochemical

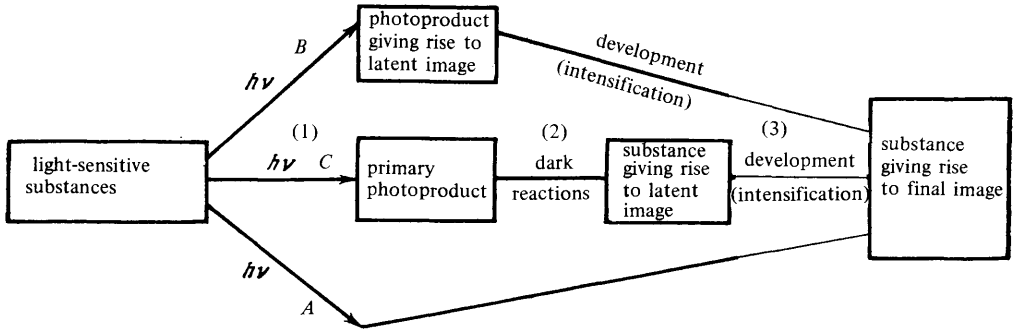


Figure 1. Schematic illustration of the production of the image when chemical non-silver photographic processes are employed.

Table 1. Photographic characteristics of light-sensitive materials whose operation is based on photochemical reactions.

No.	Material	Development (intensification)	$\Delta\lambda$, nm	Q, J cm^{-2}	R, mm^{-1}	No. of rerecording cycles	Type of recording
1	Diazotype (Refs.46,79,80)	Treatment in ammonia vapour	300—500	10^{-1} [46]	1500 [80]	1	Amplitude
2	Vesicular (Refs.81-83)	Thermal	300—500	10^{-2*} [83]	600 [82]	1	Phase
3	Light-sensitive polymers (negative) (Refs. 69,84-86)	Washing in a solvent	250—400	$5\cdot10^{-3}$ [86]	500 [84]	1	Phase relief
4	Light-sensitive polymers (positive) (Refs.69, 87-89)	Ditto	250—480	$3\cdot10^{-1}$ [89]	1400 [88]	1	Phase relief
5	Photochromic (Refs.1-21)	No development stage	250—700	10^{-2} [4,6]	3500 [6]	10^{4} (Ref.4)	Amplitude, phase, phase-amplitude
6	Photopolymerisation (Refs.35-43, 90, 91)	Washing in a solvent	280—700	10^{-3} [91]	1000 [90]	1	Phase relief
7	With physical development (Refs. 22-30, 92, 93)	Physical	300—700	10^{-7} [92]	1200 [93]	1	Amplitude
8	Free-radical (Refs. 56-63)	Optical ($\lambda > 500$)	300—500	$4\cdot10^{-4}$ [57]	5000 [56]	1	"
9	Chromium-treated colloids**	Washing in water	250—580	$2\cdot10^{-3}$ [71, 95]	4000 [96]	1	Phase relief
10	(Refs.71, 94-96)	Thermal	250—400	10^{-4} [97]	1000 [98, 99]	1	"
11	Photodeformation (Refs.97-99)	"	230—260	2 [100]	500 [100]	1	"
12	Photothermopolymerisation (Ref.100) Cyanotype (Refs.75, 101, 103)	No development stage	280—400	—	—	1	Amplitude
13	Luminescent (Refs.104-107)	Optical	150—380	10^{-4} [107]	400 [106]	Several	"
14	Photoenzymographic (Ref.102)	—	—	—	—	—	—

* Calculation based on Fig. 2 [83] for $\Delta D_{project} = 0.3$.

** Dichromated gelatin (Ed. of Translation).

processes in semiconductors, etc. We shall isolate from this large group of processes those which involve photochemical transformations in the molecule, i.e. are unimolecular or bimolecular reactions in the initial organic or inorganic compounds, and shall define them as photochemical processes for the recording of information. In the present review attention is concentrated on organic compounds.

Analysis of the activity of the light-sensitive non-silver materials known hitherto showed that processes in the following fourteen materials can be assigned to the subclass of photochemical processes for the recording of information: diazo-type materials, vesicular materials, light-sensitive polymers (positive and negative), photochromic materials, photopolymerisation materials, materials with physical development, free-radical materials, chromium-treated colloids, photodeformation materials, photothermopolymerisation cyanotype materials, luminescent materials, and photoenzymographic materials; the properties and photographic characteristics of these materials are discussed in the next Section.

II. PHOTOGRAPHIC CHARACTERISTICS OF NON-SILVER MATERIALS WHOSE ACTIVITY IS BASED ON PHOTOCHEMICAL REACTIONS

Table 1 presents the main characteristics of fourteen types of the above materials: the method of development of the latent image, the region of spectral sensitivity, the maximum values of energetic sensitivity and resolving power, the number of rerecording cycles, and the types of recording. Table 1 shows that different methods are used to develop and fix the image in non-silver light-sensitive materials of the type under consideration: treatment with a gas, "wet" development (treatment in an appropriate solution), thermal, and optical. The range of spectral sensitivity ($\Delta\lambda$) of the materials is 200–700 nm.

The energetic light sensitivity of a photographic material Q is defined as the minimum amount of energy (in J cm^{-2}) giving rise to a definite photographic effect) i.e. the change in the optical density of the image ΔD (for example $\Delta D = 1$ is adopted for materials Nos. 5 and 8, and $\Delta D = 0.2$ is adopted for material No. 7) or in the depth of the relief (0.1 and 0.2 μm for materials Nos. 10 and 11 respectively). The energetic light sensitivities of the materials listed in Table 1 are in the range 10^{-1}–10^{-7} J cm^{-2}. The resolving power $R = 400$–5000 mm^{-1} is more than enough for the majority of technical applications of the given materials. The number of rerecording cycles is 1 to 10^4; the materials permit amplitude, phase, and phase-amplitude recording.

The problems of the application of the materials are not considered in this review; they are dealt with in other reviews and monographs[3,4,15,32,36,73]. It is noteworthy that only the resolving power of these materials satisfies all the practical requirements. In terms of important characteristics such as the region of spectral sensitivity and energetic light sensitivity, these materials are greatly inferior to silver halide materials and can replace the latter only in a limited number of instances.

III. GENERAL SCHEME FOR THE KINETIC ANALYSIS OF THE PHOTOCHEMICAL STAGE IN THE RECORDING OF INFORMATION. PRINCIPAL APPROXIMATIONS

We shall consider a general scheme for the kinetic analysis of the photochemical stage in the recording of information. Since the efficiency of the photochemical process is determined by the quantum yield, it is necessary to establish how the principal photographic parameters of the light-sensitive material are related to the quantum yield, namely the energetic light sensitivity Q and the red limit of the region of spectral sensitivity λ_{lim}. Having analysed subsequently the dependence of the quantum yield of the photochemical reaction on the properties of the initial light sensitive system, we can relate Q and λ_{lim} to the initial parameters of the substance and hence can estimate the limiting values of these parameters.

The primary photochemical reaction can be unimolecular or bimolecular. The unimolecular reaction can be represented in the following form:

$$A^0 \xrightarrow{h\nu} A^*,$$
$$A^* \xrightarrow{k} B \text{ (product)},$$
$$A^* \xrightarrow{k_d} A^0,$$

where A^0 is the initial substance in the ground electronic state and A* is the initial substance in the excited state. The quantum yield in the formation of the photoproduct is

$$q_B = k/(k + k_d), \quad (1)$$

i.e. is determined by the ratio of the rate constants for the photochemical reaction (k) and for the deactivation of the excited state (k_d).

A bimolecular photochemical reaction can be regarded in the most general form as a process involving a random approach of the reacting molecules to a distance necessary for the occurrence of the reaction (this event will be called an "encounter") and the chemical reaction proper. At the instant of the "encounter" the molecules are surrounded by a cage of solvent molecules. Diffusion-controlled processes are usually understood as those whose rate is controlled by the frequency of "encounters". The mechanism of a bimolecular reaction can be represented as follows:

$$A^0 \xrightarrow{h\nu} A^*,$$
$$A^* + C \underset{k_r}{\overset{k_{diff}}{\rightleftharpoons}} [A^* \ldots C],$$
$$[A^* \ldots C] \xrightarrow{k} B \text{ (product)},$$
$$A^* \xrightarrow{k_d} A^0,$$
$$[A^* \ldots C] \xrightarrow{k_d} A^0 + C,$$

where k_{diff} is the rate constant for the enclosure of the reactants in the solvent cage and k_r the rate constant for the emergence from the cage. The quantum yield in the formation of the photoproduct is

$$q_B = \frac{k_{diff}[C]}{k_{diff}[C] + k_d} \cdot \theta_1, \quad (2)$$

where θ_1 is the probability of the reaction in the cage.

Thus the dependence of the quantum yield of the product of the primary photochemical process on the properties of the initial light-sensitive system is determined by its dependence on a number of constants. The rate constant for the photochemical reaction k is in the general case a function of the symmetry and energy $\epsilon_{S(T)}$ of the electronic state, the distribution of electron density in the excited

state, and the properties of the medium in which the reaction takes place (viscosity, temperature, etc.). For each specific photochemical reaction, different parameters among those enumerated can assume the main role, and the exact calculation from the constants for photochemical reactions is at present impossible.

According to this scheme, the rate constant k_d characterises the rate of radiative and non-radiative deactivation of the excited state. It is determined both by the properties of the reacting molecule (symmetry, spin–orbit interaction, vibronic interaction, etc.) and the properties of the matrix (temperature, viscosity, concentration of excitation quenching agents, etc.). However, if we confine ourselves to the case of viscous solutions, which are of main interest in the practical application of light sensitive materials, then many factors become insignificant and it is possible to obtain an answer to the main question—how k_d changes on passing from one compound to another. It is then assumed *a priori* that there is a possibility of synthesising compounds absorbing light and having an energetically predetermined reactive state. Theory[108] and experiment[109] showed that, for conjugated organic molecules with $\epsilon_S(T) < 20\,000$ cm^{-1} (in the estimation of the red limit of the region of spectral sensitivity this energy range is of interest), the constant k_d is determined by a non-radiative process, i.e. $k_d = k_{nr}$, where k_{nr} is the rate constant for the non-radiative deactivation of the excited state. For different compounds belonging to a single class, the constant k_{nr} is fully determined by the energy of the excited state $\epsilon_S(T)$ and the dependence of its values on $\epsilon_S(T)$ is exponential. The empirical dependence of the rate constant k_{nr}^T on the energy of the triplet state ϵ_T of aromatic compounds is described by the formula

$$k_{nr}^T = {}^0k_{nr}^T \exp(-\varepsilon_T/\varepsilon_0), \tag{3}$$

where ${}^0k_{nr}^T$ and ϵ_0 are constants within a single class of compounds and their numerical values (${}^0k_{nr}^T = 10^{7.5}$ s^{-1} and $\epsilon_0 = 1000$ cm^{-1}) have been calculated[109]. According to the theory, the above relation breaks down for $\epsilon_T \leqslant \epsilon_{vib}$.

We shall now proceed to the specific estimation of the long-wavelength limit of the region of spectral sensitivity. The region of spectral sensitivity of the material is determined by the dependence of the quantum yield in the primary photoprocess q on the frequency of the incident light, since the remaining stages in the production of the image as a rule take place in the dark. It should be noted that, only when a vibrationally unexcited singlet (or triplet) state is involved in the photochemical reaction, does the spectral sensitivity coincide with the absorption spectrum of the light-sensitive substance[110]; in many instances these spectral curves may not coincide[111]. In order to determine the red limit of the region of spectral sensitivity of materials, it is necessary to estimate the minimum energy of photons ϵ^{lim} which cause an excitation of the photochemical reaction such that the latter has an adequate quantum yield, for example $q = 10^{-1}$. This choice is arbitrary, but, for $q < 10^{-1}$, the overall light sensitivity of the material becomes low (for an insignificant or zero intensification coefficient), and the region where the material can be used is restricted.

The minimum energy of photons required for the occurrence of a unimolecular photochemical reaction ϵ_T^{lim} can be obtained from Eqn. (1) after substituting in the latter the values of k and k_{nr} as a function of the energy of the reactive state ϵ_T (in the given case the triplet state) and after solving the equation for ϵ_T when $q = 10^{-1}$. In the most general case it is probably possible to assume that, on passing from one molecule to another within a given class, the rate constant for the photoprocess is zero when the energies of the electronic state ϵ_T are smaller than the energies expended on the primary photochemical reaction $\epsilon(I)$ [i.e. $k = 0$ for $\epsilon_T < \epsilon(I)$] and, when $\epsilon_T > \epsilon(I)$, k increases with increase of ϵ_T [i.e. $k = f(\epsilon_T)$ when $\epsilon_T > \epsilon(I)$]. Unfortunately it is as a rule not known how k depends on ϵ_T. If the dependence of the rate constant k_{nr} for a non-radiative transition on the energy of the excited state ϵ_T is described by Eqn. (3), then, when account is taken of the foregoing considerations, Eqn. (1) yields the following minimum energy of the reactive triplet state:

$$\varepsilon_T^b = \varepsilon_0 \ln({}^0k_{nr}^T/9k). \tag{4}$$

In order that the above expression should have a physical significance, the following boundary condition must hold: the energy of the absorbed photon must be greater than or equal to the energy $\epsilon(I)$ required for the occurrence of the primary photochemical reaction $\epsilon_T^b \geqslant \epsilon(I)$. Consequently the red limit of the region of spectral sensitivity in photochemical processes involving the recording of information is determined by two restrictions—energetic and kinetic. If the limits of the estimate based on energetic conditions are known, it is possible to claim *a priori* that allowance for kinetic limitations can lead to a hypsochromic shift of the red limit of the region of spectral sensitivity.

For a bimolecular reaction, the minimum energy of photons required to ensure the occurrence of the reaction can be obtained analogously from Eqn. (2) having substituted in the latter k_d and θ_1 as functions of the energy of the reactive state ϵ_T.

When the reaction proceeds via a singlet molecular state, the approach to the determination of the limiting characteristics remains the same with the sole difference that ${}^0k_{nr}^T$ in Eqn. (4) is replaced by the rate constant ${}^0k_{nr}^S$, the numerical value of which is determined by the ratio ${}^0k_{nr}^S/{}^0k_{nr}^T \simeq 10^6$.[112]

In those cases where the image is determined by the absorption of light by the final products of the overall reaction (photochemical or chemical) the energetic sensitivity of light can be estimated from a formula analogous to that quoted by Jackson[18]:

$$Q = 96DE/qN\varepsilon, \tag{5}$$

where ϵ is the molar extinction coefficient of the substance (litre mole^{-1} cm^{-1}) which gives rise to the final image, E the energy of the photon in eV, D the optical density of the image ($D_0 = 0$), and N the coefficient of the intensification of the primary action of light. The maximum value of N is determined by the ratio of the reactivities of the initial substance and the photoproduct in relation to the reaction involving the intensification of the primary image.

Thus Eqn. (5) shows that the light sensitivity is determined mainly by the product qN. Evidently, for low quantum yields in the primary photoprocess q but an effective intensification process (i.e. a high value of N), the material can exhibit a high light sensitivity.

If it is assumed that the quantum yield in all primary reactions is unity, the final product has an extinction coefficient $\epsilon = 10^5$ litre mole^{-1} cm^{-1} (this is virtually the limiting value for molecular systems), and the primary image intensification stage is absent, then the limiting energetic light sensitivity of the material, calculated by Eqn. (5) for $\lambda = 400$ nm, is $Q_{D=1}^{400} = 3 \times 10^{-3}$ J cm^{-2}.

In order to estimate the red limit of the region of spectral sensitivity in specific systems by the scheme described above, it is necessary to establish beforehand the type of primary photochemical reactions in the light-sensitive materials employed and to classify these materials in terms of such reactions.

IV. CLASSIFICATION OF LIGHT-SENSITIVE MATERIALS IN TERMS OF PRIMARY PHOTOCHEMICAL REACTIONS

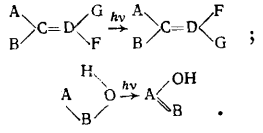
The materials will be classified and their characteristics within each group will be compared†. For this purpose, the primary photochemical reactions of the light sensitive materials listed in Table 1 were analysed. It was found that four primary photochemical reactions are characteristic of materials in this group.

I. Photoaddition:

$$A + B \xrightarrow{h\nu} AB .$$

Here and henceforth A and B are radicals, ions, or molecules. This group includes light-sensitive polymers (negative materials) and photochromic, photodeformation, and luminescent materials.

II. Photorearrangement:



Photochromic materials and materials with physical development belong to this group.

III. Phototransfer of an electron:

$$A + B \xrightarrow{h\nu} A^+ + B^- .$$

The third group includes cyanotype materials, chromium-treated colloids, materials with physical development, and photopolymerisation, photochromic, and free-radical materials.

IV. Photodissociation:

$$AB \xrightarrow{h\nu} A + B .$$

The fourth group includes diazotype and vesicular materials, light-sensitive polymers (negative or positive), and photodeformation, photochromic, photopolymerisation, and photothermopolymerisation materials with physical development.

All four possible elementary photochemical reactions employ only photochromic materials in the production of an image. This is natural, since a property common to all photochemical reactions (reversibility) is used in photochromic materials. In materials with physical development three elementary photochemical reactions are employed: photorearrangement, phototransfer of an electron, and photodissociation. The activity of photopolymerisation materials is based on two elementary photoprocesses: electron transfer and dissociation. Materials of this type cannot be synthesised on the basis of photoaddition and photoisomerisation reactions. Indeed two types of photopolymerisation are known: ionic and radical. In order to initiate polymerisation, it is necessary to generate (by irradiation with light) radicals or ions, which cannot be obtained in photoaddition and photoisomerisation reactions.

Table 2 presents the principal characteristics of materials for each elementary photochemical reaction occurring in them. Evidently materials involving different primary reactions have significantly different energetic light sensitivities, in particular materials with minimum sensitivity have been obtained on the basis of the photoaddition reaction. The observed difference is associated with the fact that the photoprocesses enumerated can generate primary products with the same or different reactivities. Because of this, in some cases there is a possibility of processes involving the intensification of the primary image, while in others there is no such possibility. It will be shown below that the type of primary photochemical reaction determines to a large extent also the red limit of the region of spectral sensitivity of materials.

Table 2.

Parameters of materials	Type of reaction			
	I	II	III	IV
R, mm^{-1}	200—3000	2000	400—5000	50—5000
q	10^{-1}—1	10^{-1}—1	10^{-1}—1	10^{-1}—1
N	1	$\geqslant 1$	$\geqslant 1$	$\geqslant 1$
Q, J cm^{-2}	10^{-1}—10^{-2}	10^{-1}—$5\cdot10^{-4}$	10^{-1}—10^{-7}	10^{-1}—10^{-4}

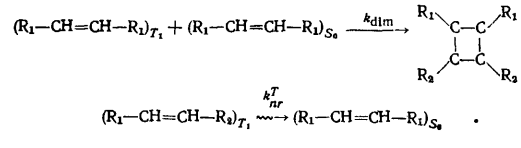
V. RELATION BETWEEN THE RED LIMIT OF THE SPECTRAL SENSITIVITY OF MATERIALS AND THE KINETIC AND SPECTROSCOPIC CONSTANTS OF LIGHT-SENSITIVE SUBSTANCES

We shall consider in succession the primary photochemical reactions enumerated above, which occur in the recording of an image on light-sensitive materials.

1. Photoaddition

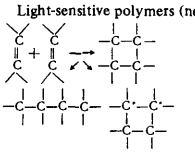
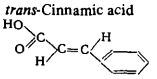
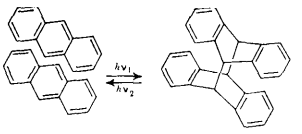
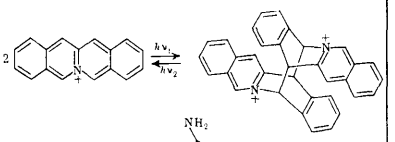
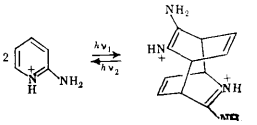
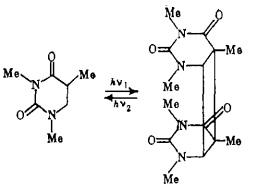
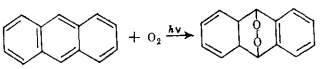
Table 3 presents the principal properties of specific light-sensitive materials in which the primary photochemical reaction is photoaddition. We shall consider photoaddition to an ethylenic double bond, which takes place, for example, in negative photoresistors based on cinnamates and constitutes a model photoaddition reaction. The transition from the primary photochemical reaction to the final parameters of the material will be discussed in relation to this reaction.

Dimerisation involving an ethylenic double bond is a bimolecular reaction in which an excited molecule is added to an unexcited molecule with formation of a cyclobutane ring. Experiments on the sensitisation of this reaction by the triplet–triplet energy transfer showed that it can proceed via an excited triplet state[123–125]. The kinetic scheme for the photodimerisation process can be formulated as follows:



† The classification of inorganic light-sensitive materials in terms of primary photoprocesses has been described[74,75] without the analysis of the limiting characteristics.

Table 3. Photoaddition.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity $\Delta\lambda$, nm*	Refs.
Light-sensitive polymers (negative)				
Cinnamic acid derivatives R_1—C(=O)—(CH=CH)$_x$—C$_6$H$_4$—R_2 R_1 — polymer chain; x = 1,2,... = 1, 2 ...		Photodimerisation involving an olefinic double bond	275**	31, 33, 69, 85, 113—115
Photochromic materials				
trans-Cinnamic acid 	ditto	ditto	λ_1<300, λ_2>300	116—117
Anthracene		Photodimerisation of aromatic hydrocarbons	λ_1=380, λ_2=280	118—120
Acridizinium and benzacridizinium salts		Photodimerisation of aromatic heterocycles	λ_1=500, λ_2=360	118
2-Aminopyridine		ditto	λ_1=310, λ_2=240	118
1,3-Dimethylthymine		»	λ_1= ~278, λ_2= ~240	118
Photodeformation materials				
Rosin	Replacement of two conjugated double bonds by single bonds		λ u.v.	118, 119
Abietic acid	Photosensitised oxygen transfer		λ u.v.	98, 99
Luminescent materials				
Anthracene		Photoaddition of oxygen	λ u.v.	104—107

* λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

** The values of λ_{max} are quoted.

There are no energetic restrictions in the dimerisation reaction, since it proceeds after each "suitable" collision of excited and unexcited molecules. It is probably possible to consider two cases of dimerisation: dimerisation controlled by diffusion and addition of molecules "prepared" beforehand in a cage of matrix molecules. The first instance occurs in reactions in liquid and gas phases and also in a solid–gas system. The second obtains in reactions of molecules in solid solutions and polymers.

The second case is characteristic of the majority of light-sensitive materials, whose activity is based on the photoaddition reaction. Only in photodeformation (abietic acid) and luminescent materials is the addition reaction diffusion-controlled. When the reacting molecules have been enclosed in cages beforehand and the bimolecular reaction proceeds after the collision of species in the cage, the quantum yield can be formulated thus:

$$q = \frac{k_{col}}{k_{col} + k_{nr}}\,\theta_2,$$

where k_{col} is the rate constant for the collision process in the cage and θ_2 is the probability of reaction on collision. If it is assumed that $\theta_2 = 1$ for the photoaddition reaction in the cage, then the overall quantum yield of

the reaction is equal to the probability of the collision of excited and unexcited molecules in the cage, whereupon $k_{dim} = k_{col}$. The constant k_{col} is determined by the mobility of the reacting molecules, i.e. ultimately by the size and shape of the cage and the dimensions of the reacting molecules, as well as the energy of the intermolecular additive–matrix interaction. In the general case, for a reaction in the cage, it is given by the formula

$$k_{col} = k^0_{col} \exp(-E/RT), \quad (6)$$

where k^0_{col} is the frequency of collisions of two molecules and E is the activation energy for the collision of molecules in the cage. The red limit of the region of spectral sensitivity of materials operating on the basis of the photoaddition reactions can be obtained in this case from Eqn. (4) after substituting in the latter $k = k_{col}$ from Eqn. (6).

For numerical estimates of values of ϵ^{lim}_T, it is necessary to know the specific values of the rate constants and activation energies E. The recombination in a radical pair incorporated in a matrix is a model addition reaction for molecules in a cage. The recombination process itself, like the addition reaction, proceeds without activation energy and the observed activation energy E is due to kinetic causes—it is the activation energy for the mutual approach of molecules. The rate constant for the recombination of radicals of the type $\dot{N}\!\!<^{Ph}_{Ph}$ has been found[126] ($k^0_{rec} = 10^{8.5}$ s^{-1}, E = 7000 cal mole^{-1}).

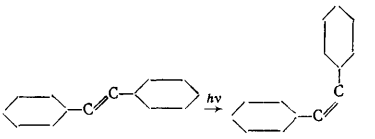
The same value of the rate constant, i.e. $k_{dim} = k_{rec}$, can probably be adopted for the addition reactions of compounds in which R_1 and R_2 are substituents such as phenyl rings. For compounds where more rigid matrices are used as the substituents, the dimerisation rate constant k_{dim} may be much smaller, mainly as a consequence of the increased activation energy for the collision process. If it is assumed that $k^0_{dim} = 10^9$ s^{-1} and E = 7 kcal mole^{-1} for all dimerisation reactions in solid solutions, then we have $\epsilon^{lim}_T = 6000$ cm^{-1} from Eqn. (4).

On photoexcitation of the system, the triplet state is formed from the singlet state as a result of the $S-T$ transformation. Since $\epsilon_{S-T} = 2000$–3000 cm^{-1} for molecules with low-lying triplet states, the red limit for the photochemical reaction involving the triplet state is defined as follows: $\nu^{lim} = \epsilon^{lim}_T + \epsilon_{ST} = 8000$ cm^{-1}, so that $\lambda_{lim} = 1250$ nm.

The dependence of the limiting energies of the triplet and singlet state ϵ_T and ϵ_S on the activation energy E for different constants k^0_{col}, $^0k^T_{nr}$, and $^0k^S_{nr}$ is illustrated in Fig. 2.

2. Photorearrangement

Table 4 lists the light-sensitive materials employing the photorearrangement reaction. The most thoroughly investigated case is that of *trans–cis* isomerisation, namely the *trans–cis* isomerisation relative to ethylenic bonds. Examples of such compounds are provided by aryl derivatives of ethylene and thioindigo dyes. The characteristics of the isomerisation of arylethylenes are in broad outline typical of the isomerisation of other classes of compounds. We shall consider the *trans–cis* isomerisation process in relation to the stilbene molecule. For stilbene and arylethylenes, it has been shown that the *trans–cis* isomerisation can proceed via both triplet[131,132] and singlet[133–135] excited states. The general process mechanism can be represented as follows:



$$trans\text{-form}^{S(T)} \xrightarrow{k_{tc}^{S(T)}} cis\text{-form}^{S_0},$$

$$trans\text{-form}^{S(T)} \xrightarrow{k_{nr}} trans\text{-form}^{S_0}, \quad (7)$$

where k_{tc} is the rate constant for the *trans–cis* isomerisation.

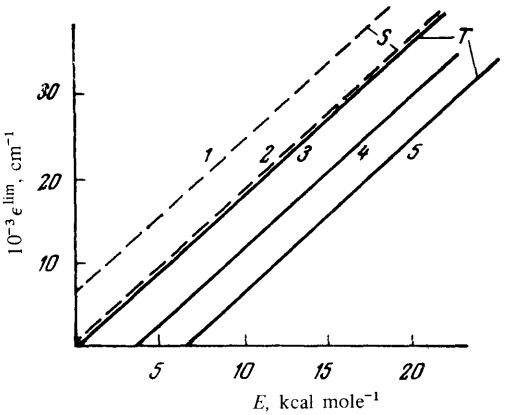


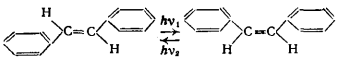
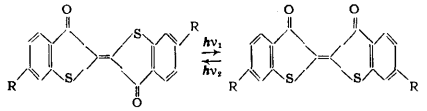
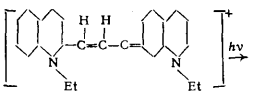
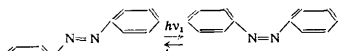
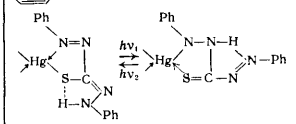
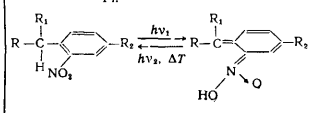
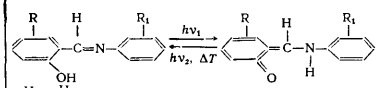
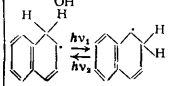
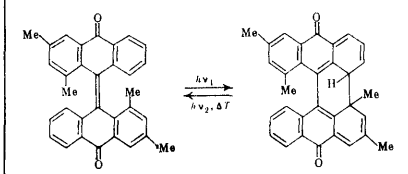
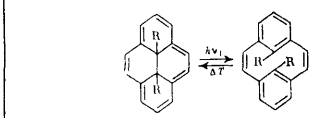
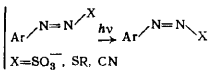
Figure 2. Dependence of the limiting energies ϵ^{lim} of the triplet and singlet states of the molecules on the activation energies; k^0_{col} (s^{-1}): 1), 4), and 5) 10^9; 2) and 3) 10^{12}; $^0k^S_{nr}$ (s^{-1}): 1) and 2) 10^{13}; $^0k^T_{nr}$ (s^{-1}): 3) and 4) $10^{7.5}$; 5) 10^{10}.

Scheme (7) shows that a molecule in the excited state can be either converted into the *cis*-form, which corresponds to the rotation of one fragment relative to the connecting bond, or it can relax to the ground state. For arylethylenes in the triplet state, rotation about the central bond (without taking into account the interaction with the medium) is virtually free from an energy barrier (its height amounts to several kcal)[136,137] and the rotation frequency of the fragment is close to the rotation frequency of the molecule as a whole. It can be assumed that, for identical matrices, the rate constant for the isomerisation of electronically excited molecules is the same as the frequency of the thermal rotation of a molecule of similar size, i.e. it can be formulated as follows:

$$k_{tc} = k^0_{tc} \exp(-E_{rot}/RT), \quad (8)$$

where E_{rot} is the activation energy for rotation determined by the interaction of the molecule with the matrix.

Table 4. Photorearrangement.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity, Δλ, nm*	References
	Photochromic materials			
Substituted ethylenes		*trans-cis* isomerisation	$\lambda_1=295$, $\lambda_2=280$	2, 9, 11, 12, 14, 16
Indigoid compounds		Ditto	$\lambda_1=510$, $\lambda_2=450$	2–4, 9, 127
Cyanine dyes		» »	565, 610 **	2
Azo-compounds		» »	$\lambda_1=319$, $\lambda_2=324$	2, 11, 14
Metal dithizonates		Tautomerism with hydrogen transfer	$\lambda_1=490$, $\lambda_2=600$	2, 4, 128, 129
Nitrobenzyl derivatives		Ditto	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=600$	2, 14
Anils		» »	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=500$	2, 4, 9, 16
Radicals formed by adhesion of hydrogen to aromatic hydrocarbons		» »	$\lambda_1=335$, $\lambda_2=385$*	130
2,4,2',4'-Tetramethylbianthrone		Valence tautomerism	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=650$	2, 11, 16
Derivatives of trans-15,16-dialkyldihydropyrene		Ditto	$\lambda_1=600$	2
Aromatic hydrocarbons		*T-T* absorption	$\lambda_1=\lambda_{u.v.}$ $\lambda_2=\lambda_{visible}$	2
	Materials with physical development			
Benzenediazosulphides Benzenediazosulphonates Benzenediazocyanides		*trans-cis*-isomerisation	<450	24, 29

* λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

** The values of λ_{max} are quoted.

Thus in making the estimate we assume that the activation energy for an electronically excited molecule is determined, regardless of the energy of the excited states, by the activation energy for the rotation of the molecules in the given matrix. On the assumption that the reaction rate constant $k = k_{tc}^{S(T)}$ is independent of the energy of the excited state $\epsilon_{S(T)}$, the red limit of the region of spectral sensitivity can be estimated from Eqn. (4) after substituting in the latter the numerical values of the reaction rate constant.

There are no data for the parameters of the rotation of aromatic molecules (benzene, naphthalene, etc.) in polymeric matrices. On the other hand, there is much information about the pre-exponential factors and activation energies for the rotation of iminoxy-radicals in

various polymers. For the estimates, we shall assume that the characteristics of the rotational motion of iminoxy-radicals simulate the corresponding parameters for the simplest aromatic compounds. This assumption is probably valid, since the dimensions of the radicals and the compounds which they simulate (for example, arylethylenes and the simplest thioindigo dyes) are approximately the same, and in both cases there is no specific additive–matrix interaction. Having assumed for the *trans–cis* isomerisation in the polymer the activation energy and pre-exponential factor obtained for the rotation of the iminoxy-radical in polystyrene (E_{rot} = 18.2 kcal mole^{-1} and $k^0_{tc} = 4\times10^{18}$ s^{-1} [138]), we can calculate from Eqn. (4), for k_{tc} derived from Eqn. (8), the quantity $\epsilon^{lim}_T = 3000$ cm^{-1} at 300 K. This result is comparable to ϵ_{vib}.

The red limit for a photochemical reaction involving the triplet state with the direct excitation of the molecule to the singlet state and subsequent $S-T$ transition to the triplet state is determined as follows: $\nu lim = \epsilon^{lim}_T + \epsilon_{ST} = 5000$ cm^{-1}; $\lambda_{lim} = 2000$ nm.

It is most probable that the red limit of the region of the spectral sensitivity obtained is too high. The main cause of this is the assumption of the absence of an internal barrier to rotation. For polymethine dyes, the activation energy increases several fold with decrease of the energy of triplet levels[139]. Allowance for this factor leads to a hypsochromic shift of the red limit.

3. Phototransfer of an Electron

Materials whose activity is based on the phototransfer of an electron are listed in Table 5. In the general form the phototransfer of an electron can be represented schematically as follows[148]:

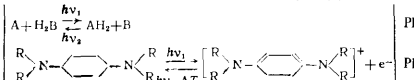
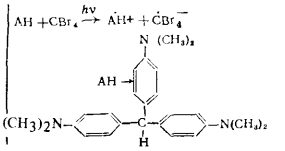
$$A^{S(T)} + H_2Y \xrightarrow{k_e} A^{\cdot}e^- + H_2Y^{\cdot+},$$
$$A^{S(T)} \xrightarrow{k^{S(T)}_{nr}} A^0,$$

where k_e is the rate constant for electron transfer.

As in photoaddition, the process consists of two stages—the mutual approach to a distance R_0 and subsequent electron transfer over this distance. It has now been established that phototransfer of an electron is a tunnel process and to a first approximation its rate constant varies exponentially with the distance. However, for the estimates in the present review, one can assume that, when $r \leq R_0$, the rate constant for electron transfer is large (the estimate yields $k_e = 10^{14}$ s^{-1} for $r < R_0$ [149]) and the probability of electron transfer over such distances $\theta_1 \simeq 1$, because the constants for the deactivation of the singlet ($k^S_{nr} = 10^{13}$ s^{-1}) and triplet ($k^T_{nr} = 10^{7.5}$ s^{-1}) states (see above) are smaller than the rate constant for electron transfer indicated above.

Thus the overall quantum yield in the phototransfer of an electron is determined by the probability of the mutual approach of the donor and acceptor to the transfer distance

Table 5. Electron phototransfer.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity Δλ, nm*	References
	Cyanotype materials			
Iron oxalate	$2Fe^{3+} + C_2O_4^{2-} \xrightarrow{h\nu} 2Fe^{2+} + 2CO_2$	Photochemical reduction	$\lambda_{u.v.}$	75, 101, 103
	Chromium-treated colloids			
Chromium-treated gelatin	Cr^{6+} + colloid $\xrightarrow{h\nu}$ Cr^{3+} + oxidised cross-linked colloid	Oxidation-reduction reaction	<580	71, 94–96
	Materials with physical development			
Fe^{3+} salts of organic acids + Pd, Pt, Rh, Ag, Au, Hg, and Cu salts	$Fe_2(C_2O_4)_3 \xrightarrow{h\nu} 2Fe(C_2O_4) + 2CO_2$ $2Fe^{2+} + Pd^{2+} \rightarrow 2Fe^{3+} + Pd^0$	Photochemical reduction	<400	24, 140, 141
Anthraquinone-2,7-disulphonate	$AQ + BH_2 \xrightarrow{h\nu} AQH(AQH_2) + BH(B)$	Ditto	$\lambda_{u.v.}$	24, 142–144
Methylene Blue	$D + BH_2 \xrightarrow{h\nu} DH(RH_2) + BH(B)$	»	$\lambda_{visible}$	24
	Photopolymerisation materials			
Dyes: Bengal Rose, Eosin, etc.	$A + RH \xrightarrow{h\nu} AH^{\cdot} + R^{\cdot}$	Photochemical reduction	$\lambda_{visible}$	76, 90, 145, 146
Peroxides + Fe^{3+}	$Fe^{3+} \xrightarrow{h\nu} Fe^{2+}$; $Fe^{2+} + H_2O_2 \rightarrow HO^{\cdot} + OH^- + Fe^{3+}$	Photochemical oxidation	$\lambda_{u.v.}$	76
	Photochromic materials			
Dyes: Thiazine, Oxazine	$A + H_2B \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} AH_2 + B$	Photochemical reduction	$\lambda_1 = \lambda_{visible}$	2
p-Phenylenediamine derivatives		Photochemical oxidation	$\lambda_1 = \lambda_{u.v.}$ $\lambda_2 = \lambda_{visible}$	147
	Free-radical materials			
Leucoform of dyes (triphenylmethane, cyanine)	$AH + CBr_4 \xrightarrow{h\nu} AH^+ + \dot{C}Br_4^-$ 	Photochemical oxidation	300–500	56–63

*λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

and can be calculated from Eqn. (2), where $c = H_2Y$ and $\theta_1 = 1$.

Two cases are possible in this reaction.

1. The distance between the donor and acceptor is small ($r \leq 5$) and the mutual approach stage is not required for the occurrence of the reactions; the process involves solely electron transfer. In this case there are no kinetic limitations, i.e. the first multiplier in Eqn. (2) is unity and the red limit of the region of spectral sensitivity is determined solely by energetic limitations: $\epsilon^{lim}_{S(T)} = \epsilon(I)$.

2. The reaction is controlled by diffusion and its quantum yield is determined by the probability of encounters. This case corresponds to low concentrations of the acceptor or a low rate constant k_{diff} for the diffusion of the donor to the acceptor. In this case the stage involving the mutual approach of the donor and acceptor is rate-limiting. The red limit of the region of spectral sensitivity is determined from Eqn. (4), which in this case assumes the following form:

$$\varepsilon^{lim}_T = \varepsilon_0 \ln (k^T_{nr}/9k_{dif}[H_2Y]) \quad . \tag{9}$$

Fig. 3 presents the dependence of ϵ^{lim}_T on $[H_2Y]$ plotted on the basis of Eqn. (9). It is noteworthy that the dependence has a physical significance only for $\epsilon^{lim}_T > \epsilon(I)$. The necessary energetic limitation of the electron phototransfer reaction $\epsilon(I)$ is determined (without taking into account the interaction with the medium)[150] from the condition:

$$\varepsilon(I) = I_{H_2Y} - Q_A - W_e, \tag{10}$$

where W_e is the energy of the Coulombic interaction of the charges in the ion pair (the dissociation energy of the ion pair), Q_A is the electron affinity of the electron acceptor, and I_{H_2Y} is the ionisation potential of the electron donor.

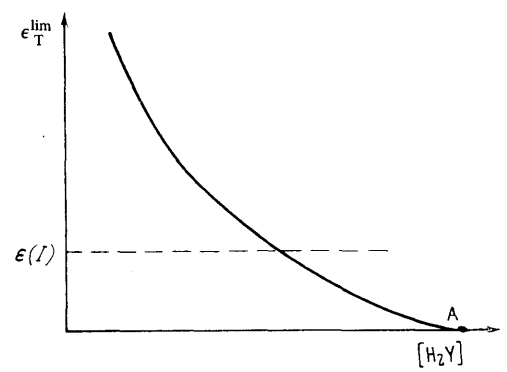


Figure 3. Dependence of ϵ^{lim}_T on the concentration of the electron donor H_2Y. $[H_2Y] = k^T_{nr}/9k_{dif}$ at point A.

Since experimental relations between k^T_{nr} and ϵ_T were used in the given study for conjugated hydrocarbons, in the estimates it is useful to employ as the electron acceptor (excited molecule) a substance in the class of conjugated hydrocarbons for which $Q_A = 0$–1.0 eV.[151]

For the zinc oxide ($I_{ZnO} = 6.6$ eV) [152]–conjugated hydrocarbon donor–acceptor pair, the estimate of the minimum value of $\epsilon(I)$ based on Eqn. (10) for $W_e = 3 - 4$ eV yields $\epsilon(I) = 1.6$ eV and correspondingly $\lambda(I) = 770$ nm.

4. Photodissociation

Table 6 presents data whose employment is based on the photodissociation reaction. This elementary reaction embraces the largest number of light sensitive materials. It has been established that the photodissociation of organic compounds can proceed via several mechanisms[162].

Dissociation into a continuum. In this case the molecule is excited directly to the repulsive state. The molecule excited from the ground to a non-bonding state decomposes during the period of one vibration, which is approximately 10^{-13} s. This mechanism of the decomposition reaction is characteristic of simple molecules (Fig. 4*a*).

Thermal or quasi-equilibrium dissociation. The molecule is excited to a bonding state, which lies above the bond dissociation energy Fig. 4*b*). After the electronic energy has been transformed into the vibrational energy of the entire molecule, the latter is concentrated in a single bond and causes its rupture. As a rule this is the weakest bond.

Non-adiabatic dissociation. In this case the electron energy is concentrated in one specific vibration (or in several vibrations). As a rule, this is the most anharmonic vibration. For example, in hydrocarbon molecules, the most anharmonic vibration is that of the C–H bond.

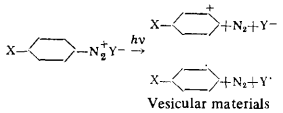
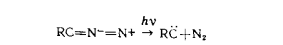
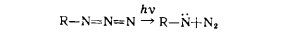
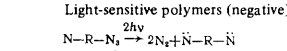
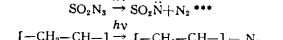
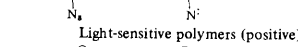
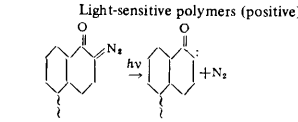
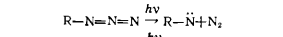
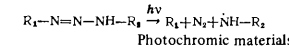
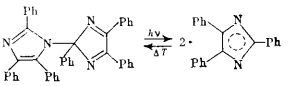
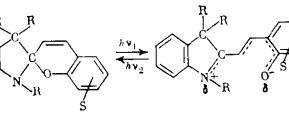
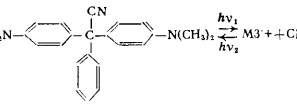
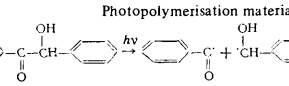
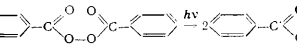
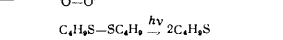
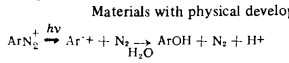
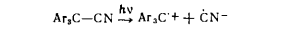
Predissociation. This dissociation mechanism obtains in complex organic molecules. The molecule is excited to a higher bonding state, i.e. the electronic excitation is delocalised over the entire molecule (Fig. 4*c*). This high bonding state intersects the repulsive state associated with any one bond and the interaction of the states leads to a transition of the molecule from a bonding to a repulsive state. This is followed by the dissociation of the given bond as a result of the concentration of the electron energy in the latter.

Dissociation involving a multistage intramolecular process. In complex molecules containing several chromophoric groups the dissociation process can consist of several intramolecular stages. In the first stage intramolecular charge transfer takes place, which results in the weakening or dissociation of one of the bonds. The next stage involves the decomposition of the unstable form into molecular fragments.

In order to determine the red limit of the region of spectral sensitivity of materials whose employment is based on the photodissociation reaction, it is necessary to examine the energetic and kinetic limitations in this reaction.

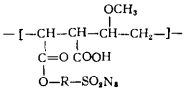
From the energetic point of view the minimum energy of the absorption of a photon, giving rise to photochemical activity, is limited by the dissociation energy of the weakest bond and in thermal dissociation of light-sensitive substances is directly equal to the energy of the weakest bond (Fig. 4*b*)[163]: $h\nu^{lim}(I) = D_{A-B} = 30$ kcal mole^{-1} = 1.3 eV, so that $\lambda_{lim}(I) = 1000$ nm. On the other hand, if the predissociation mechanism operates, the minimum energy of the photon must be about 1.5 times greater than the energy of the bond undergoing dissociation (Fig. 4*c*).

Table 6. Photodissociation.

Light-sensitive substance	Primary photochemical reaction	Type of reaction	Region of spectral sensitivity Δλ, nm*	References
	Diazotype materials			
Diazonium Salts		Heterolytic decomposition	300—500	44—46,153,154
		Homolytic decomposition		
	Vesicular materials			
Diazonium salts	Ditto	Ditto	Ditto	81
Diazo-compounds		Homolytic decomposition into a molecule and a biradical	<500	44,46,49
Aromatic and heterocyclic azides		Ditto	250—400	155
	Light-sensitive polymers (negative)			
Bisazides		»	250—400	156—159
Arylsulphonylazide group		»	240—290	86
Azide polymers		»	300**	160
	Light-sensitive polymers (positive)			
Naphthoquinone diazides		»	420**	87—89
	Photodeformation materials			
Azides		»	250—400	161
Triazenes		»	285—400	97
	Photochromic materials			
Bi-imidazolyls		Homolytic decomposition into two radicals	$\lambda_1=365$, $\lambda_2=351,574$	2,4
β-Tetrachlorooxodihydronaphthalene		»	$\lambda_1=\lambda_{u.v.}$, $\lambda_2=550$	2
Spiropyrans		Heterolytic decomposition into two ions	$\lambda_1=400$, $\lambda_2=\lambda_{u.v.}$	2,4
Derivatives of triarylmethane dyes			$\lambda_1=313$, $\lambda_2=430\,625$	2
Photodimers: of anthracene, acridizinium and benzacridizinium salts, 2-amino-pyridine, 1,3-dimethylthymine	(see photoaddition)	»		
	Photopolymerisation materials			
Carbonyls		Homolytic decomposition into two radicals	390**	73,76
Peroxides		Homolytic decomposition into two radicals	<320	76
Organic sulphur compounds		Homolytic decomposition into a molecule and a radical	340**	76
	Photothermopolymerisation materials			
Poly(butyl methacrylate), copolymer of butyl methacrylate and methacrylic acid	Tentative photodissociation of a fragment of polymer chain	Homolytic decomposition into two radicals	—	100
	Materials with physical development			
Diazonium salts		—	380—420	29,52
Leucocyanides of triphenylmethane dyes			$\lambda_{u.v.}$	24

*λ_1 represents the region of spectral sensitivity of the initial substance and λ_2 the region of spectral sensitivity for the reverse reaction.

**The values of λ_{max} are quoted.

***SO_2N_3 is the light-sensitive group of the polymer 

However, if $k_{diss} \ll k_{nr}$, then the quantum yield in the primary photochemical reaction may be close to zero even when the photon energy exceeds the bond energy. In this case kinetic limitations operate and $\lambda_{lim} < 1000$ nm. It is not possible to obtain a kinetic estimate of the red limit of spectral sensitivity owing to the lack of sufficiently well developed models of the photodissociation of complex molecules. If the photodissociation reaction proceeds by

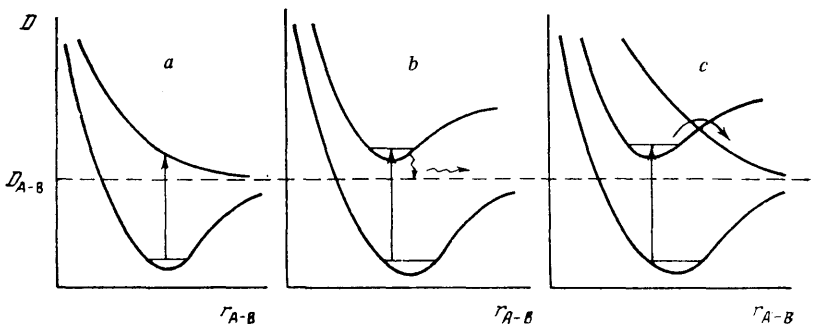


Figure 4. Mechanisms of the photodissociation of molecules: *a*) dissociation into continuum; b) thermal or quasi-equilibrium dissociation; c) predissociation. The arrows indicate the two stages of the process–conversion of electron energy into vibrational energy and bond dissociation.

dissociation into a continuum, then the condition $k_{diss} \gg k_{nr}$ holds and such photochemical reactions will have the energetic red limit calculated above.

VI. CONCLUSION

This review examines the properties of non-silver light-sensitive materials whose activity is based on photochemical reactions, analyses the nature of the primary photochemical reactions employed, and classifies the materials in terms of primary photochemical reactions. The classification shows that the type of primary photochemical reaction determines the nature of the primary photoproduct, i.e. the possibility of subsequent chemical intensification and hence the energetic light sensitivity of the material. The importance of assessing the possibility of intensifying the primary effect follows from the fact that the experimental energetic light sensitivities of such materials do not usually exceed 10^{-1} J cm^{-2}. This difference from the limiting calculated light sensitivity is apparently associated with the fact that the quantum yield of the photochemical reactions of the substances employed $q < 1$ and the extinction coefficient of the photoproduct $\epsilon < 10^5$ litre mole^{-1} cm^{-1}.

Thus the importance of seeking possible intensification processes is evident. Chemical intensification reactions are in principle possible only subject to the condition that the initial substance and the product have different reactivities. We shall consider which photochemical reactions permit further intensification.

According to Table 3, a photoaddition reaction as a rule gives rise to stable products and both the initial substance and the final product have no catalytic activity and cannot initiate oxidation-reduction or polymerisation processes. Consequently the occurrence of a chemical intensification process in such materials is unlikely.

Photorearrangement as a rule results in the formation of stable products. However, cases are known where reaction products are also formed. For example, Jonker and coworkers[24,29] found that the primary action of light may be intensified. They used the ability of the *cis*-benzenediazo-sulphides and -sulphonates, obtained as a result of *trans–cis* isomerisation, to disproportionate mercurous ions with formation of metallic mercury nuclei—centres for physical development. This made it possible to attain a light sensitivity $Q = 5 \times 10^{-4}$ J cm^{-2} for materials with physical development based on the *trans–cis* isomerisation reaction.

The phototransfer of an electron leads to the formation of products, which have reactivities markedly different from those of the starting materials and which are capable of initiating oxidation–reduction reactions, polymerisation, etc. Because of this, materials whose employment is based on electron phototransfer have the highest energetic light sensitivity—up to 10^{-7} J cm^{-2}.

Photodissociation gives rise to radicals, biradicals, or radical-ions, which can initiate polymerisation processes ensuring high values of the coefficient of the intensification of the primary action of light.

The approach proposed in this review, which takes into account both kinetic and energetic limitations in the primary photochemical reaction, has made it possible, in conjunction with several specific models, to estimate the red limit of the region of spectral sensitivity for primary photochemical reactions. However, one should note that the values obtained are only approximate. It is better to regard them as an illustration of the fact that the proposed approach permits a quantitative analysis of the properties of light sensitive materials on the basis of the characteristics of photochemical reactions.

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Catalytic Ionic Hydrogenation

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Data on the catalytic hydrogenation of unsaturated organic compounds in acid media are examined and discussed. A new method of catalytic hydrogenation in acid media, in which the catalyst activates hydrogen and the substrate is activated by the acid which converts it into a positively charged intermediate, is proposed. The role of catalysts as agents transferring hydride ions from molecular hydrogen to carbonium ions is considered.
The bibliography includes 58 references.

CONTENTS

I. Introduction 332
II. Interaction of carbonium ions with hydrogen. Hydride ion transferring agents 333
III. Homogeneous hydrogenation catalysts as agents transferring hydride ions from molecular hydrogen to carbonium ions 334
IV. Heterogeneous catalysts as hydride ion transferring agents 339

I. INTRODUCTION

Hydrogenation is one of the most general and common reactions in organic chemistry. It is widely used both in organic synthesis (among other purposes, for the preparation of important substances) and in the study of the reactivities and structures of compounds. A multiplicity of different methods for the hydrogenation of unsaturated organic compounds belonging to different classes have now been developed. Some of them, for example hydrogenation over heterogeneous catalysts, are extremely effective; they are widely used in chemistry and chemical engineering.

One of the main requirements which must be met by hydrogenation methods is selectivity, i.e. the possibility of hydrogenating some unsaturated groups in the molecule without affecting others. The majority of studies on hydrogenation have been devoted recently to the solution of this problem. The fundamental factor which determines a particular type of selectivity of the given hydrogenation method is the reaction mechanism. However, the mechanism of various hydrogenation reactions has not always been established or has been elucidated only in the very broadest outline. In particular, the determination of the mechanism of hydrogenation in the presence of heterogeneous catalysts constitutes a problem which has still not been fully solved, to a large extent because these reactions are accompanied by a number of complex physicochemical processes on the catalyst surface.

We believe that hydrogenation reactions can be classified in terms of the properties of the unsaturated substrate, which largely determine the mechanism of the given reaction, and the nature of the selectivity of the hydrogenation process can be predicted for groups of reactions based on the same property of the substrate. In this approach all the known hydrogenation processes are divided into three broad groups.

The first group comprises methods based on the ability of the unsaturated compound to be coordinated to the catalyst metal atom. It includes all hydrogenation reactions in the presence of homogeneous or heterogeneous catalysts. A common feature of the mechanism of these reactions is coordination of the unsaturated substrate to the metal or its complex, which activates hydrogen. We shall not discuss here the exact meaning of the term "coordination" and we shall only note that, whatever the mechanism of the interaction of the substrate with the catalyst, the mutual approach of the species involved in this interaction is postulated. The extensive experimental data accumulated on catalytic hydrogenation show that an increase in the number and bulk of substituents at the hydrogenated bond leads to a decrease of the rate of hydrogenation. Catalytic hydrogenation methods therefore make it possible to hydrogenate selectively less shielded multiple bonds. For example, in the series of olefins the rate of hydrogenation decreases in the sequence: terminal olefins > disubstituted ethylenes with a double bond within the chain > trisubstituted ethylenes > tetrasubstituted ethylenes.

For certain catalysts, the difference between the rates of reaction is so great that selective hydrogenation of terminal olefins is possible in the presence of olefins having a large number of substituents at the ethylenic carbon atoms. The carbonyl group and the benzene ring are hydrogenated much more slowly than the ethylenic double bond, but the shielding of the latter by bulky substituents sometimes permits the selective hydrogenation of these groups without involving the ethylenic bond. Certain catalytic systems permit the selective hydrogenation of double bonds activated by electron-accepting substituents.

One should note that catalytic hydrogenation in most cases gives rise to products of the *cis*-addition of hydrogen to the unsaturated compound.

The second large group of methods for hydrogenation processes comprises those based on the electron (or hydride ion) affinity of the unsaturated compounds. It includes methods such as reduction by active metals in alcohols, acids, and amines, reduction by complex metal hydrides, lithium tetrahydroaluminate, or sodium tetrahydroborate, boranes, or alanes, and electrochemical hydrogenation methods. A characteristic feature of the mechanisms of these reactions is initial attack on the unsaturated compound by a nucleophile—an electron or a hydride ion†; this makes it possible to combine all such reactions in a single group and to expect them to have similar selectivities in the hydrogenation of unsaturated systems.

† We believe that the hydride ion transfer process involves the overall transfer of a proton and two electrons from one molecule to another. However, the detailed mechanisms of such reactions will not be considered in the present review.

Polar groups and polarised double bonds are readily reduced by these methods. Ethylenic bonds can be reduced fairly successfully in those cases where they are conjugated to electron-accepting substituents such as carbonyl, carboxy-, nitro-, and cyano-groups, aromatic rings, and other groups. In olefins under optimum conditions there is a possibility of the selective hydrogenation of a double bond activated by an electron-accepting substituent in the presence of compounds of other types. Furthermore, the addition of aluminium and boron hydrides to olefins permits the selective hydrogenation of the terminal double bonds in the presence of double bonds within a chain or olefinic groups with branching at the ethylenic carbon atom.

The third group consists of methods for the electrophilic ionic hydrogenation‡. The reaction mechanism is based on the ability of the unsaturated compound to combine with a proton to form an active intermediate—a carbonium ion, which, by abstracting a hydride ion from a suitable donor, is converted into the hydrogenation product. For a given acidity of the medium, this reaction permits the selective hydrogenation of unsaturated compounds capable of existing in equilibrium with the corresponding carbonium ions, in the presence of other unsaturated compounds which do not form carbonium ions in the reaction medium.

For example, in acids with $H_0 \simeq -3$ (trifluoroacetic acid) the use of a hydrogen-containing silane as a hydride ion donor results in the selective hydrogenation of olefins branched at the ethylenic carbon atom. Such olefins are capable of forming tertiary alkyl cations as a result of protonation by trifluoroacetic acid; at the same time, unbranched olefins with a double bond within the chain, whose protonation might give rise to less stable secondary carbonium ions, are not hydrogenated under these conditions. The introduction of electron-donating substituents, stabilising the carbonium centre, permits the hydrogenation also of monosubstituted olefins, for example styrene, vinyl ethers, and vinyl sulphides.

The selectivity of electrophilic hydrogenation is thus fundamentally different from the selectivity of the groups of hydrogenation reactions described above, in which unsaturated substrates activated by electron-accepting substituents are hydrogenated preferentially. Yet another characteristic feature of the electrophilic ionic hydrogenation is the preferential *trans*-addition of hydrogen; in molecules with a rigid skeleton, for example, in certain steroids, *trans*-addition products are formed exclusively.

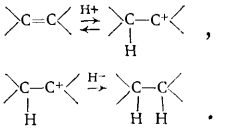
Thus all known hydrogenation methods are based on three properties of unsaturated compounds: tendency towards coordination to the catalyst metal atom, the ability to combine with a nucleophilic species (solvated electron, hydride ion, the anion of a complex hydride), and finally the tendency towards electrophilic attack—towards the initial protonation of the substrate. We believe it is difficult to imagine yet another fairly general property of unsaturated compounds which might constitute the basis of a fundamentally new hydrogenation process. It therefore appears extremely promising to combine the advantages characteristic of different groups of hydrogenation processes.

By virtue of the availability of the hydrogenating agent (molecular hydrogen), catalytic methods are greatly superior to procedures based on other hydrogenation processes. As stated above, the usual catalytic hydrogenation methods and methods based on the electron affinity of the unsaturated compound manifest similar selectivities, while the selectivity of electrophilic ionic hydrogenation is in principle unattainable when the first two methods are used. It was therefore of interest to develop a catalytic ionic hydrogenation process which would possess the advantages of catalytic methods and the selectivity of ionic hydrogenation.

‡ In contrast to this, reduction by complex metal hydrides might be called nucleophilic ionic hydrogenation.

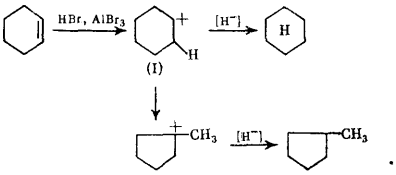
II. INTERACTION OF CARBONIUM IONS WITH HYDROGEN. HYDRIDE ION TRANSFERRING AGENTS

The mechanism of ionic hydrogenation includes two stages: protonation of the unsaturated compound with formation of an active intermediate (carbonium ion) and irreversible interaction of the latter with a hydride ion donor, leading to hydrogenation products:



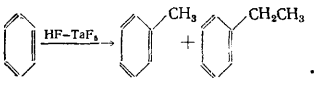
Hydrogen-containing silanes with organic substituents or hydrocarbons having a suitable structure are normally used as hydride ion donors[1]. The simplest and most readily available hydride ion donor is molecular hydrogen, but it is extremely inactive in relation to carbonium ions.

When a solution of $AlBr_3$ in cyclohexene is heated in a hydrogen atmosphere (150°C, pressure 80 atm, 26 h), only 2% of cyclohexane and 4% of its isomerisation product (methylcyclopentane) are formed[2]; the main bulk of the product consists of unidentified high-boiling hydrocarbons. The authors[2] believe that the reaction mechanism involves a stage in which a hydride ion is split off from hydrogen by a secondary carbonium ion (I), formed as an intermediate under these conditions:



A stable, i.e. relatively unreactive, cation such as triphenylcarbonium does not interact with hydrogen under the conditions indicated. A solution of $AlBr_3$ in benzene at 180°C and a hydrogen pressure of 68 atm absorbs a slight amount of hydrogen, but neither cyclohexane nor methylcyclopentane were detected in the reaction products[2].

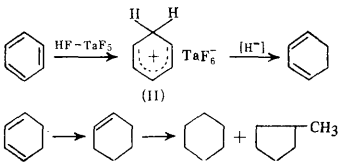
When benzene reacts with the $HF-TaF_5$ system, the main products are toluene and ethylbenzene in a yield of approximately 40% (relative to the benzene which has reacted)[3]:



The authors believe that the hydrogen required for this reaction is formed in the condensation of benzene to polycyclic compounds under the reaction conditions. When the reaction is carried out under hydrogen pressure, the yield of toluene and ethylbenzene increases by 15–25%.

The hydrogenation of benzene in the presence of the $HF-TaF_5$ system in hydrocarbons (for example in n-hexane) at 50°C leads to cyclohexane as the main product[4]. The reaction mechanism with the intermediate formation

of the carbonium ion (II) and the migration of a hydride ion towards it from hydrogen or, what is more likely, from the solvent has been proposed:



Certain cycloalkanes undergo hydrogenolysis, i.e. the cleavage of the ring with subsequent hydrogenation, in the same system at 50°C and a hydrogen pressure of approximately 15 atm.[5] Thus cyclohexane readily isomerises to methylcyclopentane, which is cleaved with formation of a mixture of t-hexyl cations. Their reduction by hydrogen leads to a mixture of isomeric hexanes. Cyclopentane gives a mixture of straight-chain pentane and isopentane. The rate of hydrogenolysis of cycloalkanes depends on the steric strain in the ring and on the nature of the carbonium ion formed during the cleavage process.

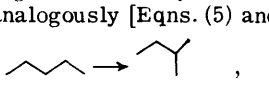
A more detailed study of the hydrogenation of benzene by hydrogen in strong acid media showed[6] that the hydrogenation proceeds at 50°C and a hydrogen pressure of approximately 30 atm in the presence of the $HF-TaF_5$, $HF-SbF_5$, $HBr-AlBr_3$, and $HCl-AlCl_3$ systems. Benzene is hydrogenated only in the presence of hydrocarbons having tertiary carbon atoms. Molecular hydrogen, unbranched alkanes, and cycloalkanes cannot serve as hydride ion donors in this reaction. Straight-chain reactions are first isomerised to isoalkanes, which are in fact the true hydride ion donors in relation to carbonium ions formed in the protonation of the benzene ring. At a hydrogen pressure >14.8 atm the reaction proceeds in the presence of catalytic amounts of isopentane, the role of hydrogen consisting in the reduction of the isopentyl cation formed from isopentane when a hydride ion is transferred to protonated benzene.

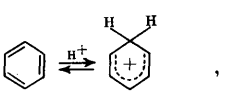
It was shown in an earlier study of the isobutane–trimethylcarbonium equilibrium in a strong acid medium[7] that this entails the reduction of the tertiary alkyl carbonium ion by hydrogen:

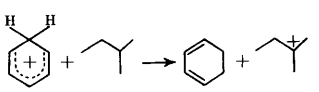
$$(CH_3)_3CH \underset{H_2}{\overset{HF,\,SbF_5}{\rightleftharpoons}} (CH_3)_3C^+SbF_6^- + H_2 .$$

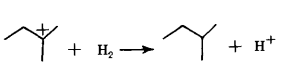
The benzyl[8], norbornyl, and methylcyclohexyl cations[9] are also reduced by hydrogen ion superacids.

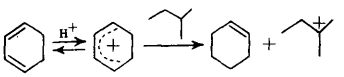
A mechanism of the hydrogenation of benzene by hydrogen in the presence of alkanes has been proposed on the basis of these data[6]: isomerisation of n-pentane to isopentane (1), protonation of benzene (2), transfer of a hydride ion from isopentane to the cationic σ-complex (3), and the reduction of the isopentyl cation by hydrogen (4). The subsequent hydrogenation of dihydrobenzene to cyclohexene takes place analogously [Eqns. (5) and (6)]:

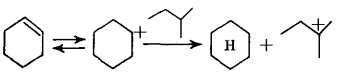

(1)


(2)


(3)

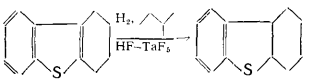

(4)


(5)

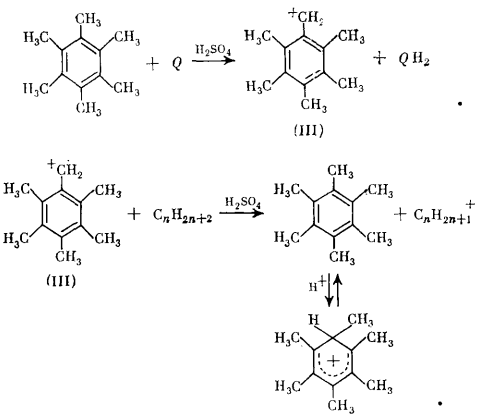

(6)

Isopentane behaves in this reaction as the catalyst—the agent which transfers a hydride ion from molecular hydrogen to carbonium ions.

It has also been shown[10] that naphthalene is hydrogenated to tetralin and the latter partly isomerises to methylindan. Anthracene is not hydrogenated under these conditions. Thiophen gives up to 40% of thiophan and dibenzothiophen is reduced to hexahydrodibenzothiophen. The same product is formed in a high yield on hydrogenation of tetrahydrodibenzothiophen in the $HF-TaF_5$ system in the presence of isopentane and hydrogen[10]:



It is of interest to note that hexamethylbenzene can serve as an agent for transferring a hydride ion from alkanes to quinones in a highly acid medium[11]. It is oxidised by the quinone to the pentamethylbenzyl cation (III), which is capable of abstracting a hydride ion from the alkane, regenerating hexamethylbenzene:



where Q = quinone.

It follows from above data that hydrogen is an extremely inactive hydride ion donor in relation to carbonium ions and, because of this, branched hydrocarbons are relatively ineffective as agents for the transfer of a hydride ion from molecular hydrogen to protonated unsaturated compounds.

III. HOMOGENEOUS HYDROGENATION CATALYSTS AS AGENTS TRANSFERRING HYDRIDE IONS FROM MOLECULAR HYDROGEN TO CARBONIUM IONS

The study of the chemistry of carbonium ions shows that one of the most characteristic reactions of these species is their ability to behave as hydride ion acceptors. The hydride mobility of hydrogen in various E–H bonds has been examined in detail in a monograph[12]. We shall only note that even strong acids such as hydrogen bromide and iodide, are capable of behaving as hydride ion donors in relation to sufficiently reactive carbonium ions.

A number of individual transition metal hydride complexes have been synthesised in recent years, many of these behaving as homogeneous hydrogenation catalysts[13,14]. Some of them are capable of transferring a coordinated hydride ion to an unsaturated substrate. Thus the isomerisation of alkyl allyl ethers to alkyl propenyl ethers catalysed by platinum hydrides[15] involves the initial addition of the platinum hydride to the double bond contrary to the Markovnikov rule, which indicates polarisation of the $Pt^{\delta+}-H^{\delta-}$ type.

It might have been expected that many transition metal hydride complexes are capable of transferring a hydride ion not only to an unsaturated compound, but also to carbonium ions; however, in the literature there are only a few isolated examples of such reactions. Thus ruthenium(IV) dihydrides reduce triphenylcarbonium, being converted into cationic complexes of ruthenium(V)[16]:

$$\underset{(IV)}{H_2RuL_3} + Ph_3C^+PF_6^- \rightarrow \underset{(V)}{(HRuL_3)^+PF_6^-} + Ph_3CH ,$$

where L = Ph_3P.

It has been asserted[17] that platinum(VI) and iridium(VII) hydride complexes reduce diphenylmethyl and triphenylmethyl cations in 60–80% sulphuric acid:

$$Ph_3C^+ \xrightarrow{(Et_3P)_2Pt(H)Cl(VI)} Ph_3CH ,$$

$$Ph_2CH^+ \xrightarrow{(Et_3PhP)_2IrH_5Cl(VII)} Ph_2CH_2 .$$

The reliability of these data[17] is open to some doubt, since a large (approximately 100-fold) excess of the metal hydride complex was used and the authors noted the decomposition of the complex in sulphuric acid. The reaction was followed solely from the change in the intensity of the band in the electronic spectrum corresponding to the absorption by the carbonium ion; the reaction products were not identified.

For the catalytic reduction of carbonium ions, the transition metal complex must be able not only to transfer a hydride ion but also to activate hydrogen with formation of a metal hydride complex in acids which are sufficiently strong to generate carbonium ions. Data demonstrating the possibility of using homogeneous catalysts to activate hydrogen in media with the required acidity for ionic hydrogenation, particularly in trifluoroacetic acid, were not available in the literature.

In 1974 the authors of the present review suggested that certain platinum-group metal complexes be used as agents for transferring a hydride ion from molecular hydrogen to stable carbonium ions[18]. The role of the catalyst in this reaction (in relation to platinum) is as follows:

(1) The platinum complex reacts with hydrogen to form the corresponding hydride complex:

$$L_2PtX_2 + H_2 \rightarrow L_2Pt(H)X + HX .$$

(2) The hydride complex then reacts with the carbonium ion, formed from the substrate in the acid medium, and converts it into the corresponding hydrocarbon:

$$L_2Pt(H)X + \diagdown\!\!\diagup C^+X^- \rightarrow L_2PtX_2 + \diagdown\!\!\diagup CH .$$

Triphenyl- and diphenyl-methanols are not reduced in trifluoroacetic acid by platinum hydride complexes, either in equimolar proportions or with a 100-fold excess of hydride, but, when the reaction is carried out under hydrogen pressure, triphenyl- or diphenyl-methanes are formed in yields exceeding 1 mole per mole of the catalyst. Consequently in trifluoroacetic acid these complexes are capable of activating molecular hydrogen and of transferring it in the form of hydride ions to stable carbonium ions.

The results of the study of the influence of the ligands and the central metal atom on the activity of catalysts in the reduction of triphenylmethanol are presented in Table 1. Comparison of data obtained for catalysts Nos. 4, 7, and 8 shows that, depending on the nature of the metal, the activity of the catalyst decreases in the sequence Pt > Pd > Ni.

Thus the possibility of using homogeneous hydrogenation catalysts (platinum, palladium, and nickel complexes of phosphine) to activate hydrogen in strong acid media and to reduce stable carbonium ions has been demonstrated.

Ruthenium salts also catalyse the reduction of triphenylmethanol by hydrogen in an acid medium[19]. In concentrated hydrochloric acid at a hydrogen pressure of 100 atm and 80°C (28 h) triphenylmethanol is converted in the presence of $RuCl_3$ into 1-(diphenylmethyl)-4-(triphenylmethyl)benzene (VIII) in 97% yield (4.2 moles per mole of the catalyst):

$$Ph_3COH \xrightarrow{HCl} Ph_3C^+ \xrightarrow{H_2,RuCl_3} Ph_3CH ,$$

$$Ph_3CH + Ph_3C^+ \rightarrow \underset{(VIII)}{Ph_2CH{-}C_6H_4{-}CPh_3} .$$

Evidently Ph_3C^+ attacks the triphenylmethane formed on reduction, giving rise to (VIII), which is stable in hydrochloric acid.

Table 1. Reduction of Ph_3CCH (0.3–0.4 g) in CF_3COOH (3 ml) (amount of catalyst 0.04–0.05 g, p_{H_2} = 100 atm, 20°C, 150 h).[18]

No.	Catalyst	Yield of Ph_3CH, mole/mole of catalyst
1	*cis*-$(Ph_3P)_2Pt(OCOCF_3)_2$	39
2	*cis*-$(Et_3P)_2Pt(OCOCF_3)_2$	27
3	*trans*-$(Ph_3P)_2Pt(H)Cl$	23
4	*cis*-$(Ph_3P)_2PtCl_2$	19
5	*cis*-$(Et_3P)_2PtCl_2$	19
6	*cis*-$(n\text{-}Bu_3P)_2PtCl_2$	14
7	*cis*-$(Ph_3P)_2PdCl_2$	15
8	*cis*-$(Ph_3P)_2NiCl_2$	10
9	*trans*-$(n\text{-}Bu_3P)_2PtCl_2$	5

The interaction between triphenylmethanol and hydrogen in trifluoroacetic acid in the presence of $RuCl_3$ leads to triphenylmethane in 96% yield. Other ruthenium salts, such as the acetate and trifluoroacetate, also catalyse the hydrogenolysis of triphenylmethanol, and are more active than $RuCl_3$. Thus under identical conditions $RuCl_3$, ruthenium acetate, and ruthenium trifluoroacetate give rise to 68, 87, and 97% of triphenylmethane. Among ruthenium salts, the trifluoroacetate is the most active. When this catalyst is used, the reduction of Ph_3C^+ is accelerated with increase of temperature. The yield of triphenylmethane was 26% (5 moles per mole of the catalyst) at 20°C, 78% (14 moles per mole of catalyst) at 50°C, and 96% (18 moles per mole of the catalyst) at 80°C. At a hydrogen pressure of approximately 1 atm, there is no reduction but, when the pressure is raised from 5 to 90 atm, the yield of triphenylmethane increases from 35 to 98%. The results show that the ruthenium salts investigated are capable of catalysing the transfer of a hydride ion from hydrogen to the carbonium ion.

The authors of the present review showed recently[20] that certain phosphine complexes of iridium (IX) also catalyse the reduction of triphenylmethanol in an acid medium, the iridium trihydride complex being the most active:

$$Ph_3COH \xrightarrow[70^\circ C,\ p_{H_2}=100\ atm]{L_3IrH_nX_{3-n}(IX),\ CF_3COOH} Ph_3CH ,$$

$$L = Ph_3P;\ X = Cl;\ n = 1-3 .$$

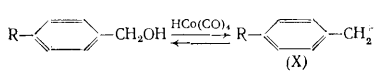
The ability of certain hydrogenation catalysts to activate hydrogen in an acid medium and to transfer it in the form of hydride ions to carbonium ions made it possible to propose a new mechanism for catalytic hydrogenation, in which the catalyst activates hydrogen and the unsaturated substrate is activated by the solvent—an acid, which converts it into the active intermediate (the carbonium ion). This permits catalytic hydrogenation with a selectivity characteristic of electrophilic ionic hydrogenation.

1. Catalytic Ionic Reduction of Alcohols

The relative rate of homogeneous reduction of substituted benzyl alcohols under hydroformylation conditions in the presence of cobalt tetracarbonyl hydride decreases in the following sequence of substituents[21]:

$$p\text{-}OCH_3 > p\text{-}CH_3 > m\text{-}CH_3 > p\text{-}C(CH_3)_3 > H > p\text{-}Cl > m\text{-}OCH_3 > m\text{-}CF_3.$$

This sequence corresponds to that expected for reactions with the intermediate participation of carbonium ions (X): it is suggested that they are formed from benzyl alcohols under the influence of the acid $HCo(CO)_4$:



(X)

The mechanism of the reduction of carbonium ions was not established in the above investigation.

It has been found[22] that, in trifluoroacetic acid under hydrogen pressure and in the presence of phosphine complexes of platinum, a primary alcohol (2-ethylhexanol) and a secondary alcohol (cyclohexanol) are not reduced, while tertiary alcohols (tri-n-butylmethanol and 1-methylcyclohexanol) are converted under these conditions into the corresponding hydrocarbons. The yield of 5-n-butylnonane and methylcyclohexane were 56 and 80% respectively under identical conditions. Thus, when hydrogen is used as the hydride ion donor and phosphine complexes of platinum are used as hydride ion transferring agents, there is a possibility of the selective catalytic ionic hydrogenolysis of tertiary alcohols.

The influence of certain factors on the reduction of tertiary alcohols has been studied[22] in relation to 1-methylcyclohexanol. Methylcyclohexane is formed only when the reaction mixture contains simultaneously an alochol, trifluoroacetic acid, hydrogen, and the catalyst. Methylcyclohexane is the only product of the reduction of methylcyclohexanol; skeletal isomerisation products were never detected. After the reaction, the mixture remains homogeneous and metallic platinum is not formed. This reaction is catalytic. When bistriphenylphosphineplatinum bistrifluoroacetate is used as the catalyst in trifluoroacetic acid (hydrogen pressure 200 atm, 50°C, 35 h), the catalytic yield of methylcyclohexane is 103 moles per mole of the catalyst. After the removal of volatile mixture components, the reuse of the catalyst gives rise to similar results: the yield after 25 h under analogous conditions is 73 moles per mole of the catalyst.

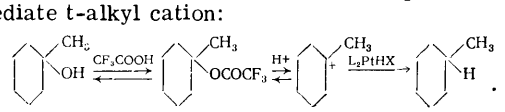
In the reduction of methylcyclohexanol, as in the reduction of triphenylmethanol, $(Ph_3P)_2Pt(OCOCF_3)_2$ is the most active of the catalysts investigated. The platinum hydride chloride and dichloride complexes exhibit similar but smaller activities. The phosphine complexes of palladium and nickel are almost inactive in the hydrogenolysis of both tertiary and secondary aliphatic alcohols.

The reduction of 1-methylcyclohexanol is greatly influenced by the solvent (Table 2). In neutral and weakly acid media (tetrahydrofuran, acetic acid, and formic acid) the reduction of 1-methylcyclohexanol is not observed. The increase of the polarity of the medium on passing from benzene to nitrobenzene and the increase of the concentration of trifluoroacetic acid appreciably increase the yield of methylcyclohexane.

Table 2. Reduction of 1-methylcyclohexanol (0.2 g) in the presence of trifluoroacetic acid (0.4 ml), the solvent (2 ml), and the $(PPh_3)_2PtCl_2$ catalyst (0.05 g) (p_{H_2} = 100 atm, 27 h, 50°C).[22]

Solvent	Yield of methylcyclohexane, %
Tetrahydrofuran	0
Acetic acid	0
Formic acid	0
Benzene	5
Toluene	6
Chloroform	14
Nitrobenzene	32
Trifluoroacetic acid–toluene (1:1)	35
Trifluoroacetic acid	96

The results permit the conclusion that the reduction of tertiary alcohols under these conditions involves hydride ion transfer from the platinum hydride complex to the intermediate t-alkyl cation:



The reduction of tertiary alcohols alone in the presence of secondary and primary alcohols confirms the ionic reaction mechanism, since in trifluoroacetic acid only tertiary alcohols are in equilibrium with the corresponding alkyl carbonium ions. In the above reaction mechanism the function of the catalyst is restricted to the activation of hydrogen, while the substrate is activated by being converted into a carbonium ion.

Ruthenium salts activate via an analogous mechanism the selective reduction of a tertiary alcohol (methylcyclohexanol) in the presence of a secondary alcohol (cyclohexanol)[19].

Thus many homogeneous hydrogenation catalysts are capable of catalysing the reduction of tertiary alcohols, and the same selectivity is observed as in the ionic hydrogenation by the silane–trifluoroacetic acid system.

2. Catalytic Ionic Hydrogenation of Olefins

Protic or Lewis acids are usually employed in homogeneous hydrogenation processes to rupture the carbon–metal σ-bond. They also facilitate the dissociation of the

ligand with liberation of a vacant site in the coordination sphere of the metal as a result of the coordination of the acid to the ligand or to the metal atom. Even in those cases where there is a possibility, in principle, of the formation of carbonium ions in the reaction [for example, in the homogeneous hydrogenation of cyclohexene with the aid of $RhCl(PPh_3)_3$ in the presence of aluminium bromide[23] or in the homogeneous hydrogenation of a series of olefins catalysed by $Rh(OCOCH_3)(PPh_3)_3$ in the presence of toluene-*p*-sulphonic acid[24]], their involvement in the reaction has not so far been discussed.

The homogeneous hydrogenation of olefins via an ionic mechanism has been described[25]. Data for the homogeneous hydrogenation of olefins in the presence of ruthenium trifluoroacetate are presented in Table 3. Evidently, when the reaction is carried out in toluene, a disubstituted ethylene (cyclohexene) is hydrogenated, while a trisubstituted ethylene (1-methylcyclohexene) does not react; the relative reactivities of these olefins in trifluoroacetic acid are reversed. Consequently, the hydrogenation of olefins in the solvents investigated proceeds via different mechanisms.

Table 3. Hydrogenation of olefins (0.1 g) in the presence of the $Ru(OCOCF_3)_3$ catalyst (0.05 g) (p_{H_2} = 85 atm, 50°C, 20 h).[25]

Olefin	Yield of saturated hydrogenation products			
	%	mole/mole of catalyst	%	mole/mole of catalyst
	in CH_3COOH		in toluene	
Cyclohexene	0	0	55	9
1-Methylcyclohexene	46	6	0	0
1,2-Dimethylcyclohexane	14	1.5	—	—
Tetramethylethylene	13	2	—	—

When the reaction takes place in toluene, the usual homogeneous hydrogenation, involving the coordination of the olefin to the ruthenium atom, occurs. Ruthenium homogeneous hydrogenation catalysts are known to be capable of the selective hydrogenation of terminal double bonds in compounds containing double bonds also within the chain or branches at ethylenic carbon atoms[26]. In trifluoroacetic acid methylcyclohexene is hydrogenated, while cyclohexene is not, which conflicts with the above rule and, in order to explain it, another hydrogenation mechanism, an ionic mechanism, must be resorted to. Since only tertiary alkyl carbonium ions are capable of existing in trifluoroacetic acid, the selectivity observed in this case can be readily accounted for from the standpoint of an ionic hydrogenation mechanism, involving the transfer of a hydride ion from the reduced form of the catalyst to the carbonium ion. One should note that even tetrastituted olefins—tetramethylethylene and 1,2-dimethylcyclohexene—are hydrogenated under these conditions. This is the first instance of the homogeneous hydrogenation of tetrasubstituted olefins catalysed by ruthenium compounds.

As in the reduction of alcohols, it was found that the hydrogenation of olefins occurs only when the reaction mixture contains all the components: the olefin, trifluoroacetic acid, the catalyst, and hydrogen. One should also note that the mixture remains homogeneous during hydrogenation and that the catalysts are insensitive to oxygen and atmospheric moisture.

The use of phosphine complexes of platinum as catalysts also permits the catalytic ionic hydrogenation of olefins. This reaction occurs only in trifluoroacetic acid; in toluene, in acetic and formic acids, in the benzene–methanol mixture, and in nitrobenzene with added hydrochloric acid the formation of alkanes is not observed.

As in the reduction of triphenylmethanol, in the hydrogenation of olefins bistriphenylphosphineplatinum bistrifluoroacetate is the more active catalyst. The results for the hydrogenation of a series of olefins in its presence are presented in Table 4. Evidently substitution of hydrogen atoms at the ethylenic bond by methyl groups has a small influence on the hydrogenation process. It is noteworthy that, in contrast to the data in Table 3, in this case the cyclohexene is also hydrogenated. Presumably the hydrogenation of cyclohexene occurs at the instant of the protonation of the substrate and some of the cyclohexyl carbonium ions have sufficient time to split off a hydride ion from the platinum hydride and to be converted into cyclohexane, while others combine irreversibly with the trifluoroacetate anion, forming cyclohexyl trifluoroacetate, which is incapable of further reduction. Indeed, with increase of the reaction time under the conditions indicated in Table 4, the yield of cyclohexane does not increase, while in the reaction of olefins branched at an ethylenic carbon atom the yield of the hydrogenation products continues to rise.

Table 4. Hydrogenation of olefins (0.1 g) in the presence of the $(Ph_3P)_2Pt(OCOCF_3)_2$ catalyst (0.02 g) and CF_3COOH (1 ml) (p_{H_2} = 100 atm, 50°C, 20 h).[25]

No.	Olefin	Yield of alkane	
		%	mole/mole of catalyst
1	Tetramethylethylene	84	50
2	1,2-Dimethylcyclopentane	56	30
3	1,2-Dimethylcyclohexene	41	22
4	1-Methylcyclohexene	45	23
5	Cyclohexene	35	20

The above data confirm the homogeneous catalytic ionic hydrogenation mechanism which involves a transfer of a hydride ion from the metal hydride complex to the carbonium ion. The ease of hydrogenation of unsaturated compounds is in this case determined by the stability of the corresponding carbonium ions and not by their tendency to coordinate to the metal atom. This leads to easier hydrogenation of trisubstituted olefins compared with olefins containing a terminal double bond or a double bond within the chain without a branch at the ethylenic carbon atom. This type of selectivity of hydrogenation is not attainable, in principle, when any other catalytic hydrogenation method is used.

3. Catalytic Ionic Hydrogenation of Carbonyl Compounds

The homogeneous hydrogenation of carbonyl compounds has been developed to a much lesser extent than the hydrogenation of olefins. The phosphine complexes of cobalt,

iridium, and rhodium may be mentioned as catalysts for the homogeneous hydrogenation of carbonyl compounds [27]. All these catalysts are capable of initiating the reduction of other functional groups as well. The following substrate activity series is then observed: olefins with a terminal double bond > disubstituted ethylenes with a double bond within the chain > trisubstituted ethylenes > aldehydes > ketones.

When homogeneous hydrogenation catalysts are used, the carbonyl group must be activated. Thus $H_3Ir(PPh_3)_3$ is an effective catalyst for the hydrogenation of aldehydes to alcohols only in acetic acid [28]. The cationic hydrides $RhH_2L_2S_2^+$ [L = PPh_3, PPh_2CH_3, $PPh(CH_3)_2$, or $P(CH_3)_3$; S is the solvent], in the presence of small amounts of water as a promoting agent, are capable of hydrogenating the carbonyl group of ketones under mild conditions [29]. It has been shown [29] that the neutral complexes $RhHL_2S_2$ do not reduce carbonyl compounds. Hydrogenation occurs only when HBF_4 is added to these catalysts, i.e. when the carbonyl group is activated either by an excess of acid or by the complex itself.

The above data show that the catalytic hydrogenation of the carbonyl group under mild conditions requires its activation by protic or Lewis acids.

Carbonyl compounds are readily reduced by hydrogen-containing silanes in trifluoroacetic acid and the mechanism of this reaction involves a stage in which the hydride ion is transferred from the silane to the intermediate carboxonium ion (XI): [1]

$$R_2C{=}O \xrightleftharpoons{CF_3COOH} \underset{(XI)}{[R_2C{=}OH]^+} \xrightarrow{R_3SiH} R_2CH{-}OH .$$

Table 5. Dependence of the yield of isopropyl trifluoroacetate on the catalyst (~0.1 g of acetone, ~0.02 g of catalyst, 3 ml of CF_3COOH, p_{H_2} = 85 atm, 30 h, 50°C). [30]

Catalyst*	Yield	
	%	mole/mole of catalyst
$(PPh_3)_2PtCl_2$	80	63
$(PPh_3)_2Pt(OCOCF_3)_2$	34	27
$(PPh_3)_2PdCl_2$	⩽1	—
$(PPh_3)_2NiCl_2$	⩽1	—

*There is no hydrogenation in the absence of the catalyst.

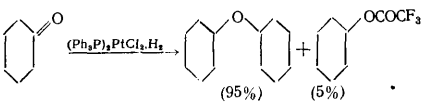
It has been shown [30] that phosphine complexes of platinum, which do not catalyse the homogeneous hydrogenation of carbonyl compounds, acquire this capacity in trifluoroacetic acid. In the ionic hydrogenation of acetone by silane and trifluoroacetic acid a mixture of 60% of isopropyl alcohol (in the form of isopropyl trifluoroacetate) and 25% of di-isopropyl ether is formed. The catalytic ionic hydrogenation of acetone gives rise to only one product–isopropyl trifluoroacetate. Data for the dependence of the yield on the nature of the catalyst are presented in Table 5. An increase of the acidity of the medium leads to an increase of the yield of the hydrogenation product (Table 6); in the absence of acid there is no hydrogenation. When trifluoroacetic acid is replaced by formic or acetic acid, the hydrogenation of acetone slows down. Under the same conditions, the yields of isopropyl trifluoroacetate, formate, and acetate, are 45, 32, and about 10% respectively.

Thus, in the homogeneous catalytic ionic hydrogenation of acetone the highest yields of product (isopropyl trifluoroacetate) were obtained when trifluoroacetic acid was used as the proton donor and solvent and the catalyst and hydride ion transferring agent was bistriphenylphosphine-platinum dichloride. The rate of ionic hydrogenation increases with increase of temperature, hydrogen pressure, duration of heating, and acidity with the medium.

Table 6. Dependence of the yield of isopropyl trifluoroacetate on the amount of trifluoroacetic acid [~0.1 g of acetone, 0.02 g of $(Ph_3P)_2PtCl_2$, p_{H_2} = 85 atm, 55°C, 23 g]. [30]

Composition of solvent, ml		Yield, %	Composition of solvent, ml		Yield, %
CF_3COOH	benzene		CF_3COOH	benzene	
0	3	0	1	2	31
0.3	2.7	5	3	0	45

As in ionic hydrogenation by the $R_2SiH-CF_3COOH$ system, in the catalytic ionic hydrogenation cyclohexanone is reduced much faster than acetone. Thus the complete reduction of cyclohexanone at 50°C and a hydrogen pressure of 85 atm takes place over a period of 21 h, whereas acetone is hydrogenated over a period of 40 h under the same conditions. The reaction gives rise to a mixture of dicyclohexyl ether (95%) and cyclohexyl trifluoroacetate (5%):

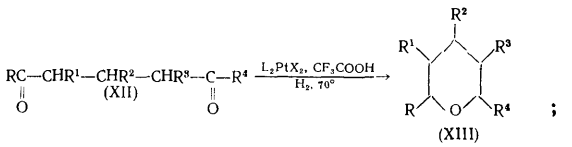


Catalytic homogeneous ionic hydrogenation of cyclohexanone can serve as a preparative method for the synthesis of dicyclohexyl ether, while other methods for its formation give low yields. For example, one of the known methods for the synthesis of this ether, from cyclohexanol and cyclohexene in hydrofluoric acid, gives only 12% of dicyclohexyl ether [31], while the yield in ionic hydrogenation by the $Et_3SiH-CF_3COOH$ system is 15%. [1]

The catalytic ionic hydrogenation of n-butyraldehyde results in the formation of only one product—n-butyl trifluoroacetate [30]. A mixture of 33% of dibutyl ether and 60% of n-butyl trifluoroacetate is obtained in the ionic hydrogenation of n-butyraldehyde by the $Et_3SiH-CF_3COOH$ system [1]. n-Butyraldehyde is hydrogenated faster than acetone. At 50°C and a hydrogen pressure of 85 atm the yields of isopropyl and n-butyl trifluoroacetates after 22 h are 42 and 67% respectively. The catalytic ionic hydrogenation of benzaldehyde gave benzyl trifluoroacetate in approximately 70% yield [30]. The yield of dibenzyl ether in the reduction of benzaldehyde by silane was 80%. [1]

The catalytic ionic hydrogenation of aromatic ketones, like their ionic hydrogenation by silanes, involves the more far-reaching reduction of the carbonyl group to the methylene group, which can be accounted for by the stability of carbonium ions in which a benzene ring adjoins the carbonium centre [30]. When benzophenone was reduced under a hydrogen pressure of 150 atm at 60°C over a period of 135 h, diphenylmethane was isolated in 93% yield. It was found [32] that, in the catalytic ionic

hydrogenation of acyclic and bicyclic 1,5-dicarbonyl compounds (XII), the corresponding tetrahydropyrans (XIII) are formed in high yields:



(XII) (XIII)

$RR^1=R^3R^4=(CH_2)_4$, $R^2=H$ (85%);
$R=R^4=C_6H_5$, $R^1=R^3=H$, $R^2=CH_3$ (97%);
$R=R^4=C_6H_5$, $R^1=R^3=CH_3$, $R^2=H$ (80%);
$R=R^2=R^4=C_6H_5$, $R^1=R^3=H$ (82%) .

The above method for the hydrogenation of 1,5-diketones is suitable also for the synthesis of tetrahydropyrans, which are of interest as plasticisers and solvents. The methods described previously for their synthesis are preparatively difficult, because in most cases they involve the addition of various compounds to the double bond of dihydropyrans, which are relatively difficult to obtain.

IV. HETEROGENECUS CATALYSTS AS HYDRIDE ICN TRANSFERRING AGENTS

Hydrogenation in the presence of heterogeneous catalysts still remains the most widely used hydrogenation procedure in industry and laboratory practice. It is highly efficient and usually presents no difficulties. The determination of the mechanism of hydrogenation in the presence of heterogeneous catalysts is extremely difficult, largely because hydrogenation is accompanied by phenomena occurring on the surface of the catalyst.

The main role of the catalysts consists in the activation of molecular hydrogen and the substrate. According to the generally accepted theory of Horiuchi and Polanyi [33], the process can be divided into the following stages:

(a) $Cat + H_2 \rightleftharpoons Cat.HH$ (adsorption of hydrogen);
(b) $Cat.HH + S \rightleftharpoons Cat.HH.S$ (adsorption of substrate);
(c) $Cat.HH.S \rightleftharpoons Cat.H.SH$ (hydrogenation);
(d) $Cat.H.SH \rightleftharpoons Cat.SH_2$;
(e) $Cat.SH_2 \rightleftharpoons Cat + SH_2$ (desorption of product).

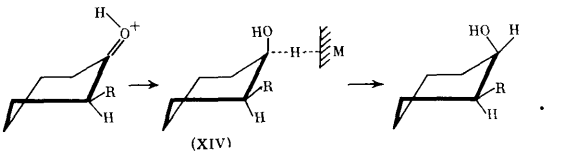
(Here Cat is the catalyst and S the substrate). It follows from the above scheme that the hydrogen activated by the catalyst adds in steps to the adsorbed substrate via the stage with a semihydrogenated state. As a rule stage (c) or (d) is rate-limiting.

The nature of the activation of hydrogen on the surface of the transition metal is still not clear, although its investigation has remained in the centre of attention of many investigators [34-36]. Without going into the details of this complex field, we shall only note that it has now come to be regarded as established than an M–H bond is formed on the metal surface [37]. The removal of hydrogen from the metal takes place via both homolytic and heterolytic mechanisms, depending on the nature of the substrate. If the substrate is a positively charged species, for example, a carbonium ion, then chemisorbed hydrogen can be transferred to the substrate in the form of a hydride ion. The reaction can then be represented by the usual scheme for ionic hydrogenation, as in the homogeneous catalytic hydrogenation in acid media (see Section III):

$$S + H^+ \rightleftarrows SH^+ ;$$
$$Cat + H_2 \rightleftarrows Cat \cdot HH ;$$
$$Cat \cdot HH + SH^+ \rightleftarrows CatH^+ + SH_2 ;$$
$$CatH^+ \rightleftarrows Cat + H^+ .$$

Under these conditions hydrogen is activated by the catalyst and the substrate by the acid, which converts it into a cation. The catalyst behaves as an agent transferring a hydride ion from molecular hydrogen to the substrate.

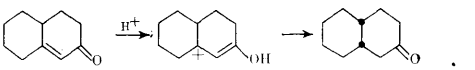
This section deals with hydrogenation reactions occurring on heterogeneous catalysts in acid media, for which an ionic mechanism has been suggested. The hypothesis of a possible ionic hydrogenation mechanism on heterogeneous catalysts was first put forward by Brewster [38] in 1954. In order to explain the influence of the medium on the stereochemistry of the hydrogenation of α-substituted cyclohexanones, he suggested that a protonated form of the ketone (XIV), coordinated in such a way that the bulky substituent (the metal) occupies a sterically less hindered equatorial position, exists in an acid medium on the catalyst surface. The hydride transfer from the catalyst to the protonated form of the ketone leads to axial alcohols:



(XIV)

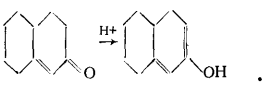
McQuillin [39,40], who studied the hydrogenation of cholestenone and testosterone over Pd/C and PtC_2 in various solvents, also found that the stereochemistry of the reaction product (the formation of 5α- or 5β-steroids) depends on the polarity of the medium. In order to account for the stereochemical results in an acid medium, he adopted Brewster's hypothesis of an ionic hydrogenation mechanism.

The concept of hydride transfer from the catalyst surface was used to interpret data obtained in the hydrogenation of a series of unsaturated cyclopropanes [41]. When $\Delta^{1,9}$-2-octalinone is hydrogenated over Pt/C or Pt/C in media with pH < 2, mainly *cis*-2-decalinone (XV) is obtained [42-44]. It is suggested that at the above pH values the protonated form (XVI) is formed as an intermediate and is more effectively adsorbed on the catalyst surface than the initial ketone:



(XVI) (XV)

Coordination of the metal from the sterically less hindered side of the carbocycle ensures a direction of attack by the hydride ion on the adsorbed carbonium ion which leads to (XV). It has been noted [42-44], however, that a similar stereochemical result can be obtained in the hydrogenation of the homoannular dienol (XVII), which can isomerise in an acid medium:



(XVII)

At low concentrations of ketones the rate of their hydrogenation over PtO_2 greatly increases on passing from acetic to trifluoroacetic acid or when strong acids (for example, $HClO_4$) are added to acetic acid [45]. Assuming the possibility that the reaction in strong acids proceeds via either one of the two mechanisms mentioned above, i.e. with formation of carboxonium ions or homoannular enols, Peterson and Casey [45] gave preference to the reaction mechanism involving the enol. They believe that this view is confirmed by the hydrogenolysis of t-butyl alcohol

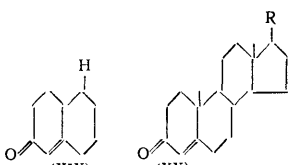
over PtO_2 in trifluoroacetic acid, which proceeds, in their view, via the hydrogenation of the isobutene in equilibrium with the initial alcohol. The equilibrium involves the intermediate formation of the t-alkyl cation (XVIII), but the possibility of the transfer of a hydride ion from the catalyst to the carbonium ion is not considered:

$$(CH_3)_3COH \overset{CF_3COOH}{\rightleftharpoons} (CH_3)_3COCOCF_3 \rightleftarrows (CH_3)_3C^+ \rightleftarrows (CH_3)_2C{=}CH_2 .$$
(XVIII)

The hydrogenation of $\Delta^{8,9}$-dihydropimaric acid over PtO_2 in acetic acid with formation of *trans,anti,trans*-tetrahydropimaric acid (instead of the expected *trans,anti,cis*-acid) was explained by a carbonium ion reaction mechanism [46].

The accelerating effect of the addition of acids (HCl and $HClO_4$) to aqueous solutions of methanol and acetic acid in the hydrogenation of nitrobenzene, acetophenone, and cyclohexene over Pt/C was explained by the formation of protonated species [47].

The ideas developed in the studies quoted above are hypothetical and are open to many objections. Firstly, the acidity of the solvents employed is insufficient for the formation of carbonium ions in the absence of the catalyst, which, however, does not rule out the possibility of the protonation of the unsaturated compound already coordinated to the catalyst. It may be that the acid has an activating effect on the catalyst, altering its properties, and not on the substrate [46]. Secondly, on the basis of the stereochemistry of the hydrogenation products, one cannot decide whether the reaction proceeds via an ionic mechanism, since the stereochemical result of heterogeneous hydrogenation is a consequence of several factors: the adsorption of the unsaturated substrate alters its geometry, which therefore entails a change in the torsional strain and intramolecular interactions; there is a possibility of the isomerisation of the substrate on the catalyst; furthermore, the surface of the catalyst is not planar, as assumed in the classical theory [49]. For example, in the study of the hydrogenation of the enones (XIX) and (XX) in acids a very large difference was observed between the stereoselectivities (i.e. between the ratios of the *cis*- and *trans*-products) when the catalyst and hydrogenation conditions were altered [50]. This effect for similar compounds cannot be accounted for solely by the formation of protonated species.

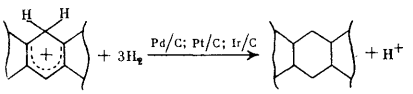


(XIX) (XX)

The reduction of stable carbonium ions can serve as direct evidence for the possibility of an ionic hydrogenation mechanism. It was observed in 1975 [51] that the hydrogenation of the triphenylcarbonium cation formed from triphenylmethanol in trifluoroacetic acid over Pt/C at 50 atm leads to triphenylmethane. This reaction can take place also over other catalysts, namely PtO_2 and Pd/C. In non-polar solvents, for example, in ether, there is no hydrogenation of triphenylmethanol.

It was later shown [52] that the catalytic hydrogenation of the triphenylcarbonium ion can take place not only in acids, but also in aprotic solvents, for example, in acetic anhydride over Pt/C, Pd/C, Ir/C, and Rh/C at 27 atm. Subsequently several more studies were published in which convincing data are presented concerning the possibility of an ionic hydrogenation mechanism on heterogeneous catalysts.

Wristers [52] observed a very large increase in the rate of hydrogenation of aromatic compounds, for example, benzene, mesitylene, hexamethylbenzene, *p*-di-(t-butyl)-benzene, and ethyl phenyl ether over Pt/C, Ir/C, and Pd/C in the presence of superacids $HF-BF_3$ or $HF-TaF_5$ (Table 7). It was found that the main product of the hydrogenation of mesitylene is 1,3,5-trimethylcyclohexane; other trimethylcyclohexane isomers are also formed, as well as insignificant amounts of alkanes with nine carbon atoms. In the hydrogenation of different aromatic hydrocarbons the rate increases with increasing concentration of the protonated aromatic compound (XXI):



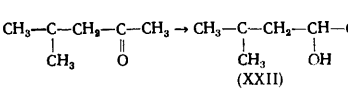
(XXI)

It has been suggested [52] that the catalyst initially activates hydrogen. The subsequent interaction of the activated hydrogen with the carbonium ion, i.e. with the cationic σ-complex (XXI), leads to the formation of a hydrocarbon and a positively charged metal. The interaction of the latter with molecular hydrogen regenerates the species with an M–H bond and the proton.

Table 7. Hydrogenation of mesitylene (0.1 mole) in acid [52].

Acid (moles)	Catalyst (5% on charcoal), g	$t_{1/2}$, min	Relative increase of rate for acid-catalysed reaction
Without acid	Pd; 1.0	12 720	1
HF (2,2)	Pd; 1.0	88	144
HF (2,3) + BF_3 (0,23)	Pd, 1.0	3.5	3630
HF (2,3) + TaF_5 (0,20)	Pd, 1.0	4.5	2830
Without acid	Ir; 1.8	1 300	1
HF (2,2) + TaF_5 (0,20)	Ir; 1.8	8.5	153
Without acid	Pt; 1.83	299	1
HF (2,4) + TaF_5 (0,20)	Pt; 1.83	22	14

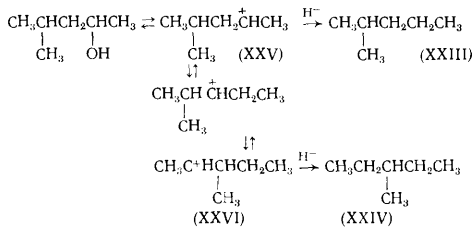
The formation of saturated products characteristic of reactions occurring with participation of carbonium ions, particularly alkylation and isomerisation reactions [53], was observed in the hydrogenation of a number of aromatic hydrocarbons over PtO_2 and RuO_2 in anhydrous hydrogen fluoride [53]. For example, the hydrogenation of benzene leads to 92% of cyclohexane as well as a small amount of cyclohexylbenzene and bicyclohexyl; the hydrogenation of *m*- and *p*-xylenes gives rise to six isomeric dimethylcyclohexanes, etc. It has also been shown [53] that PtO_2 catalyses the hydrogenation of 4-methylpentan-2-one to the corresponding alcohol (XXII) in a mixture of HF with ether:



(XXII)

In a highly acid medium (anhydrous HF) the alcohol (XXII) undergoes further reduction to a mixture of hydrocarbons (XXIII) and (XXIV). This result may be expected for the

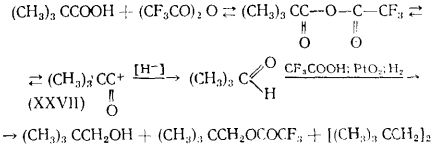
intermediate involvement of the carbonium ions (XXV) and (XXVI) in the reaction



Under the conditions indicated, cyclohexanone is reduced to a mixture of cyclohexane and methylcyclopentane. Electronegative substituents suppress hydrogenation. On the basis of these data, the author[53] believes that hydrogenation proceeds via hydride ion transfer from hydrogen on the surface of the catalyst to the intermediate carbonium ion.

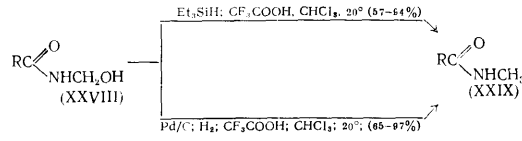
The use of anhydrous HF as the solvent, in which there is a possibility of ionic processes, permits the hydrogenation of even carboxylic acids—the class of compounds which are most difficult to hydrogenate. However, the reaction requires fairly severe conditions (300 atm) and a considerable amount of PtO_2. Dodecanecarboxylic acid is hydrogenated to a mixture of 21% of dodecane, 42% of dodecyl ether, and 6% of dodecyl dodecanoate. Acetic anhydride gives rise to ethyl acetate and diethyl ether. Succinic anhydride and oxalic acids are not reduced. It has been suggested[53] that acylium ions behave in this instance as hydride ion acceptors.

In trifluoroacetic acid, which is a weaker acid than anhydrous HF, carboxylic acids are not reduced over PtO_2. Acylium ions cannot apparently be formed in this solvent. However, the authors of the present review found[54] that, in the presence of equimolar amounts of trifluoroacetic anhydride, pivalic acid is reduced to a mixture of neopentyl alcohol, dineopentyl ether, and neopentyl trifluoroacetate in trifluoroacetic acid over PtO_2. The products of the reaction of the CF_3CO group are not formed under these conditions. The reaction evidently proceeds via the mixed anhydride of pivalic and trifluoroacetic acids, which dissociates with formation of the pivaloyl cation[53] (XXVII). The latter is reduced with abstraction of a hydride ion from the hydrogen activated by the catalyst:



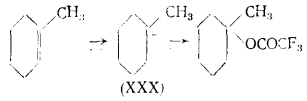
The reduction of pivalic acid in mixtures with trifluoroacetic anhydride by the triethylsilane–CF_3COOH system proceeds analogously[56]. As stated above, this system is widely used in ionic hydrogenation reactions.

N-Hydroxymethylamides of carboxylic acids (XXVIII) are converted into *N*-methylamides (XXIX) just as readily under the influence of triethylsilane as in hydrogenation in the presence of the Pd/C heterogeneous catalyst in trifluoroacetic acid[57]:



The ease of reduction of the amides (XXVIII) can be explained by the fact that the corresponding cations $RCONHCH_2^+$ are stabilised by conjugation with the free electron pair of the nitrogen atom.

A study of the competing hydrogenation of cyclohexene and 1-methylcyclohexene over Pd/C revealed[58] a change in the hydrogenation selectivity as a function of the acidity of the medium. In acetic acid both olefins are quantitatively hydrogenated, the hydrogenation of methylcyclohexene beginning only after all the cyclohexene has reacted. In trifluoroacetic acid only cyclohexene is hydrogenated, while methylcyclohexane was not detected in the reaction products. An increase of the acidity of the medium by the addition of 10% of toluene-*p*-sulphonic acid to trifluoroacetic acid leads to the quantitative hydrogenation of methylcyclohexene, while cyclohexene is hydrogenated only to the extent of 43%. These data are consistent with the ionic mechanism of the hydrogenation of methylcyclohexene under the conditions indicated. Indeed in trifluoroacetic acid methylcyclohexene combines with the acid almost quantitatively, being converted into the corresponding trifluoroacetate:



The equilibrium concentration of the carbonium ion (XXX) is low, and the adduct of hydrogen and palladium is probably a less active hydride ion donor than triethylsilane or ruthenium and platinum complexes (see Section III), and is incapable of reducing methylcyclohexene under these conditions. The addition of toluene-*p*-sulphonic acid increases sharply the concentration of carbonium (XXX) and promotes ionic hydrogenation. Under these conditions, cyclohexene combines irreversibly with CF_3COOH to form cyclohexyl trifluoroacetate, which entails a decrease of the yield of the hydrogenation product (cyclohexane).

On the basis of the foregoing, one may conclude that hydrogenation on heterogeneous catalysts in fairly acid media can proceed via an ionic mechanism, the catalysts behaving as hydride ion transferring agents.

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Catalytic ionic hydrogenation constitutes a new procedure for catalytic hydrogenation in which the unsaturated substrate is activated by the solvent (acid), which converts it into a protonated form (a carbonium ion), while the catalyst activates hydrogen and transfers it in the form of a hydride ion to the cation formed. This process permits catalytic hydrogenation with a selectivity characteristic of ionic hydrogenation reactions. There is reason to believe that many of the known hydrogenation catalysts can undergo a change in the mechanism of their action in media where there is a possibility of the formation of active protonated forms of unsaturated substrates and can behave as ionic hydrogenation catalysts.

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The Synthesis and Structure of Telluranes

I.D.Sadekov, A.Ya.Bushkov, and V.I.Minkin

Data concerning the methods for the synthesis of organic derivatives of tellurium—σ- and π-telluranes—are surveyed and described systematically. Problems of the electronic and steric structures of their molecules, the results of structural determinations, quantum-chemical calculations, and experiments by spectroscopic and other physical research methods are examined. The bibliography includes 214 references.

CONTENTS

I. Introduction 343
II. The synthesis of σ-telluranes 343
III. The synthesis of π-telluranes 353
IV. The structure of organic derivatives of tellurium(IV) 353

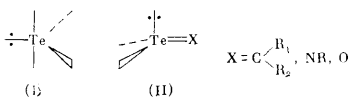
I. INTRODUCTION

The chemistry of organotellurium compounds has been investigated in considerably less detail than the chemistry of organic compounds of higher neighbours of tellurium in the Periodic Table—sulphur and selenium. The studies by Lederer and Morgan in the 1920s (see the relevant reviews[1,2]) made an important contribution to the field of organotellurium chemistry and in essence established it as a separate branch of the chemistry of organoelemental compounds. However, subsequently there was a decrease of activity in research on the methods of synthesis and reactions of organic compounds of tellurium. In the last 10–15 years there has been a renewal of interest in the organic chemistry of tellurium and there has been a sharp increase of the number of publications in this field. Most of them are described systematically in a review[2] and also in periodic collections[3,4]. Finally, a separate monograph devoted to the organic chemistry of tellurium has been published recently[5].

The study of the synthesis, reactions, and structures of various organotellurium compounds is being prosecuted on an increasing scale. It is now necessary to examine in detail data for organotellurium chemistry differentiated into individual classes rather than surveying the results for the entire field of such chemistry.

This review is devoted to tetra- and tri-coordinate organic derivatives of tellurium–telluranes. In tellurane structures the tellurium atom expands its electronic valence shell to ten electrons (or five electron pairs). The ability to form stable compounds in this hypervalent state is also manifested by sulphur and selenium, but there is no doubt that it is shown most strikingly by tellurium. The latter not only gives rise to stable π-telluranes (π-sulphuranes and π-selenuranes are as a rule also entirely stable) but also σ-telluranes. In contrast to their tellurium analogues, σ-type sulphuranes are usually stable only in cyclic structures[6-8].

The difference between σ- and π-telluranes is that in the former all five valence electron pairs occupy localised σ orbitals (I), while in π-telluranes one electron pair of tellurium forms a π bond with a neighbouring element in the Second Period (II).



(I) (II)

In agreement with predictions of valence shell electron pair repulsion theory[9], σ- and π-telluranes have different bond configurations at the central tellurium atoms, which is responsible for large differences between their physical properties and reactivities. Nor is there any similarity between the methods of synthesis of these compounds. Because of this, data for σ- and π-telluranes are examined in separate sections of the review. Initially a systematic account is given of the methods of synthesis of different telluranes and then the results of experimental and theoretical studies on their structures and reactivities are discussed.

II. THE SYNTHESIS OF σ-TELLURANES

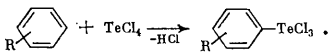
In the series of σ-telluranes (I) we shall examine below only true organotellurium compounds, i.e. those in which at least one of the four σ bonds is linked to a carbon atom. In terms of the number of such bonds, it is convenient to subdivide σ-telluranes into mono-, di-, and tetra-organo-derivatives. Such subdivision is particularly useful, since the synthetic approaches to compounds of these types are significantly different.

1. METHODS OF SYNTHESIS OF MONOORGANO-DERIVATIVES OF TELLURIUM(IV)

The most important monoorgano-derivatives of tellurium(IV) are the trihalides, the methods of synthesis of which are extremely varied.

(a) Telluration of an Aromatic Ring

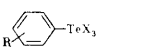
The direct method of synthesis of aryltellurium trichlorides—the telluration reaction (1)—is based on the interaction of $TeCl_4$ with benzene derivatives having fairly powerful electron-donating substituents. This reaction was achieved by Rust[10] as early as 1897 and was later investigated by Rohrbaech[11] and Lederer[12], but a correct interpretation of the structures of the compounds obtained was given only by Morgan[13,14]. When equimolar amounts of tellurium tetrachloride and phenetole were allowed to react in dry chloroform, *p*-ethoxyphenyltellurium trichloride was obtained[13]. Anisole, certain other alkyl aryl ethers, and other compounds also undergo this reaction (Table 1)[15-18]:



(I.1)

On the other hand, *p*-nitroanisole, the aromatic ring of which is highly deactivated by the nitro-group, does not react in this way[14].

Table 1. Mono-organo-derivatives of tellurium(IV) of the type $RTeX_3$.

R	X	M.p., °C	Methods of preparation	Yield, %	Refs.
Compounds of the type 					
H	Cl	215—217	(I.4)—(I.9)	69—98	45, 48, 49, 50, 52
H	Br	228—229	(I.9)	44	54
H	I	190—195	(I.9)	27	54
2-CH_3	Br	165—167	(I.9)	75	182
3-CH_3	Cl	165,5—168	(I.8)	60	50
4-CH_3	Cl	187—188	(I.4), (I.8), (I.9)	70	45, 50, 54
4-CH_3	Br	224—226	(I.9)	33, 86	54, 55
4-CH_3	I	179—180	(I.9)	54, 66	54, 55
4-OCH_3	F	176—178	(I.14)	—	26
4-OCH_3	Cl	191—193	(I.1)	90	14
4-OCH_3	Br	189—190	(I.9)	100	14, 17
4-OCH_3	I	132—133	(I.9)	93	17
4-OC_2H_5	F	204	(I.14)	—	26
4-OC_2H_5	Cl	182—183	(I.1)	92	13
4-OC_2H_5	Br	205—208	(I.9)	100	17
4-OC_2H_5	I	133—134	(I.9)	100	17
4-OC_3H_7	Cl	174	(I.1)	76	18
4-OC_4H_9	Cl	169	(I.1)	85	18
4-OC_6H_5	Cl	160—161	(I.1)	87	16
4-OC_6H_5	Br	206—207	(I.9)	100	17
4-OC_6H_5	I	160—161	(I.9)	100	17
4-$OCOCH_3$	Cl	195	(I.1)	64	18
4-$OCOC_2H_5$	Cl	198	(I.1)	58	18
2-(4′$CH_3C_6H_4O$)	Cl	180—185	(I.4)	80	44
2-(4′-$HOOCC_6H_4O$)	Cl	205—206	(I.4)	—	44
4-OH	Cl	223—225	(I.1)	84	15
4-OH	I	140—150	(I.12)	97	17
4-$NHCOCH_3$	Cl	—	(I.1)	—	15
2-SC_6H_5	Cl	213—215	(I.4)	81	17
4-SCH_3	Cl	188—190	(I.1)	51	18
4-SC_6H_5	Cl	165—166	(I.1)	42	17
4-SC_6H_5	Br	206—207	(I.9)	100	17
4-SC_6H_5	I	180	(I.9)	100	17
3-F	Cl	205—206	(I.4), (I.9)	94, 100	18, 174
3-F	Br	220—222	(I.9)	100	174
4-F	Cl	241—242	(I.9)	100	174
4-F	Br	265—267	(I.9)	100	174
3-Cl	Cl	210—211	(I.4)	95	55
4-Cl	Cl	225	(I.4)	96	18
4-Cl	Br	241	(I.9)	94	55
4-Cl	I	189—190	(I.9)	70	55
3-Br	Cl	193—194	(I.4)	92	55
4-Br	Cl	220	(I.1), (I.4) (I.8)	38, 95, 50	24, 18, 50
4-Br	Br	237	(I.9)	90	55
4-Br	I	176—180	(I.9)	63	55
2-CHO	Cl	195—200	(I.9)	95	182
3-NO_2	Cl	170—172	(I.4)	64	18
4-NO_2	Cl	193—195	(I.4)	56	18
2,3-C_4H_4	Cl	177—181	(I.1), (I.4)	24, 96	18, 17
2,3-C_4H_4	Br	159—160	(I.9)	100	17
2,3-C_4H_4	I	133	(I.9)	100	17
3,4-C_4H_4	Cl	200—202	(I.4)	85	46
3,4-C_4H_4	Br	212—215	(I.9)	100	56
2-Fluorenyltellurium trichloride	Cl	255 (decomp.)	(I.1)	53	18
3-Fluoranthyltellurium trichloride	Cl	241—243	(I.1)	18	18
2,4-$(OCH_3)_2$	Cl	155—156	(I.1)	68	13
3,4-$(OCH_3)_2$	Cl	181	(I.1)	81	13, 18
3-OH, 4-OCH_3	Cl	157—158	(I.1)	—	13
2-CH_3, 4-OCH_3	Cl	154	(I.1)	—	14
3-CH_3, 4-OCH_3	Cl	232—233	(I.1)	—	14
2-OCH_3, 5-CH_3	Cl	135	(I.1)	—	14
2-OCH_3, 5-Br	Cl	184	(I.1)	—	14
2-OCH_3, 5-Br	Br	153	(I.9)	—	14
2,3,4,5,6-F_5	Cl	—	(I.4)	—	47
Aliphatic compounds of the type $RTeX_3$					
CH_3	F	—	(I.12)	—	59
CH_3	Cl	137—139	(I.9)	63	51
CH_3	Br	140	(I.9)	—	52
CH_3	I	175—178	(I.9)	77	53
C_2H_5	Cl	114—115	(I.9)	75	183
C_2H_5	Br	138—140	(I.9)	77	53
C_2H_5	I	178—180	(I.9)	58	53
—CH(CH_3)—COOH	Br	139—141	(I.9)	—	14
$—CH_2CHClCH_3$	Cl	—	(I.2)	—	40
$—CH_2CH_2Cl$	Cl	118	(I.2)	—	41
$—CH_2CHClCH_2CH_3$	Cl	—	(I.2)	—	40
	Cl	111—114	(I.2)	—	37
	I	175—190	(I.11)	88	38
$—CH=C(Cl)C_6H_5$	Cl	205—215	(I.4)	94	43
$—C=C_6H_5=C(Cl)C_6H_5$	Cl	125—128	(I.4)	70	43

The telluration of an aromatic ring by tellurium tetrachloride is a typical electrophilic substitution reaction. It proceeds only when the benzene ring is strongly activated by electron-donating substituents and the electrophile is probably the cation $TeCl_3^+$. The tendency of $TeCl_4$ to undergo ionisation of the type $TeCl_3^+Cl^-$ or $TeCl_3^+TeCl_5^-$ in the crystalline phase and in solution is confirmed by Raman spectroscopic[19,20] and conductimetric[21] data. The stabilisation of the cation $TeCl_3^+$ on formation of tellurium tetrachloride complexes with Lewis acids, particularly with $AlCl_3$ in the form of $TeCl_3^+AlCl_4^-$,[22,23] was used by Bergman[24], who was able to achieve the interaction with tellurium tetrachloride, in the presence of catalytic amounts of $AlCl_3$, of a number of compounds (benzene, toluene) which had previously been believed to be inert in relation to this reagent. This gave small yields of the corresponding aryltellurium trichlorides (see Section 2 for a description of the synthesis of diaryltellurium dichlorides by this method). By carrying the reaction between benzene and tellurium tetrachloride in the presence of a twofold–threefold excess of $AlCl_3$, Günther et al.[25] later obtained phenyltellurium trichloride (isolated as the ditelluride), diphenyltellurium dichloride, and triphenyltelluronium chloride, depending on the reaction time.

In an early study Morgan already showed that the $TeCl_3$ group enters exclusively in the *p*-position (evidently owing to its large size) relative to the electron-donating substituent in the benzene ring, occupying the *o*-position only if the *p*-position is already occupied[13]. This was demonstrated by the fact that, when di-(*p*-ethoxyphenyl) ditelluride—the product of the reduction of the corresponding tellurium trichloride obtained by the reaction of $TeCl_4$ with phenetole—is treated with nitric acid, *p*-nitrophenetole is formed exclusively. The high selectivity of *p*-substitution by the trichlorotelluro-group in reactions of monosubstituted benzenes with tellurium tetrachloride has also been confirmed by infrared and ^1H NMR spectroscopic data[16,26]. The high selectivity of the telluration reaction and the fact that only one $TeCl_3$ group can be introduced into the ring during it constitute an appreciable difference between this process and the mercuration reaction in which the formation of polymercurated products is a normal phenomenon[27].

The study of the telluration reaction, starting with early investigations, involved a gradual expansion of the range of compounds with electron-donating functions which can be made to undergo this reaction—alkyl aryl ethers and then thioethers[17,18], acetanilide[15], etc. As already stated, compounds with a smaller π-electron density in the aromatic ring (benzene, toluene) could be made to react with $TeCl_4$ only by enhancing the electrophilic properties of the latter as a result of the formation of the complex $TeCl_3^+AlCl_4^-$. On the other hand, when the most powerful electron-donating substituent (the dimethylamino-group) is introduced into the aromatic ring, the corresponding telluration product cannot be obtained, since dimethylaniline forms a complex with tellurium tetrachloride (for its composition and reactions, see Section 2). For the same reason, *C*-derivatives are not formed with $TeCl_4$ by other nitrogen-containing bases: aromatic amines[28,29], pyridines[30-32], quinolines[31], acridines[31], and Schiff bases[33]. In contrast to these compounds, certain polycyclic hydrocarbons (naphthalene, fluorene, and fluoranthene) readily interact with tellurium tetrachloride without additional activation of its rings by electron-donating substituents and form respectively 1-naphthyl-, 2-fluorenyl-, and 3-fluoranthyltellurium trichlorides[18].

The synthesis of other aryltellurium trihalides—tribromides, and tri-iodides—by direct telluration is difficult

owing to the lower reactivity of the corresponding tellurium tetrahalides compared with the tetrachloride. The results of a study[34] where it is claimed that in the interaction of tellurium tetrabromide with benzoquinone, naphthoquinone, anthraquinone, and pyrrole the corresponding tellurium tribromides were isolated therefore require additional confirmation.

The possibilities of the telluration reaction are far from exhausted: hitherto, the main tellurating agent has been tellurium tetrachloride, but, by analogy with mercuration and thallation reactions, in which mercury and particularly thallium halide are relatively inactive, the study of the possibility of employing instead of $TeCl_4$ another tellurating agent, for example tellurium tetra-acetate or tetrakistrifluoroacetate, may extend the region where the direct telluration reaction is applicable.

(b) Telluration of Aliphatic Compounds

Organotellurium trichlorides can be synthesised also by the interaction of tellurium tetrachloride with aliphatic compounds containing active methyl and methylene groups[35]:

$$RCOCH_2R' + TeCl_4 \xrightarrow{-HCl} RCOCH(TeCl_3)R' .$$

The early publications by Morgan and coworkers[36] contain interesting but insufficiently firmly demonstrated data concerning the interaction of tellurium tetrachloride with acetic anhydride. One of the possible pathways in this reaction, according to the authors, involves the formation of a mixture of trichlorotelluroacetic acid Cl_3TeCH_2COOH, its anhydride $(Cl_3TeCH_2CO)_2O$, and methylenebis(tellurium trichloride) $CH_2(TeCl_3)_2$. The pathways followed in the formation of the latter are, however, obscure and the reliability of the structure attributed to it is open to doubt.

The ability of tellurium tetrachloride to react with homologues of acetic anhydride diminishes rapidly with increase in the size of the hydrocarbon chain. Whereas trichlorotelluropropionic acid was obtained in the reaction with propionic anhydride and identified as the ditelluride, the reactions with butyric and isovaleric anhydrides involve the reduction of tellurium tetrachloride and the products formed could not be identified[14].

(c) The Addition of $TeCl_4$ to Multiple Bonds

Organotellurium trichlorides can also be obtained by the electrophilic addition of tellurium tetrachloride to a double bond:

$$R{-}CH{=}CH{-}R' + TeCl_4 \rightarrow R{-}\underset{TeCl_3}{CH}{-}CHCl{-}R' \quad (I.2)$$

Campos and Petragnani[37,38] showed that tellurium tetrachloride reacts with cyclohexene in carbon tetrachloride, yielding 2-chlorocyclohexyltellurium trichloride. On the other hand, styrene, di-isobutene, and 1,4-diphenylbuta-1,3-diene only reduce tellurium tetrachloride to tellurium in carbon tetrachloride[38]. It is of interest to note that $TeCl_4$ is reduced to tellurium also when cyclohexene interacts with tellurium tetrachloride in the absence of a solvent[38,39]. Tellurium tetrachloride can add also to propene[40,41], giving rise to 2-chloropropyltellurium chloride or di-(2-chloropropyl)tellurium dichloride, depending on the reaction conditions. Earlier data for the addition of $TeCl_4$ to butene[42], where the formation of only two isomeric di(chlorobutyl)tellurium dichlorides was postulated and the formation of 2-chlorobutyltellurium trichloride was ruled out, were later revised[40].

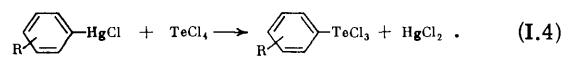
Tellurium tetrachloride adds comparatively readily also to a triple bond, forming substituted 2-chlorovinyltellurium trichlorides[43]:

$$C_6H_5C{\equiv}CR + TeCl_4 \rightarrow C_6H_5\underset{Cl}{C}{=}\underset{R}{C}{-}TeCl_3 . \quad (I.3)$$

On the whole, one should note that the addition of the tetrahalides and other tellurium compounds to multiple bonds has still been little investigated.

(d) Exchange Reactions of Organoelemental Compounds with $TeCl_4$

In order to obtain organotellurium trichlorides by this method, organic mercury compounds are usually employed. Thus the commonest method for the synthesis of aryltellurium trichlorides[44] is based on the interaction of arylmercury chlorides with tellurium tetrachloride:



(I.4)

The best solvent in this case is dioxan, which forms a complex with mercury(II) chloride, precipitated on cooling the reaction mass. The $ArTeCl_3$ derivatives obtained in this way are usually contaminated by a small amount of mercury(II) chloride, which necessitates their careful purification. In contrast to direct telluration, which leads exclusively to *p*-substituted $ArTeCl_6$ derivatives with electron-donating substituents in the aromatic ring, this method makes it possible to obtain compounds with any relative disposition of substituents, including electron-accepting substituents[17,18,44-47].

Organic compounds of lead[48] and tin[49] have been used recently to synthesise $ArTeCl_3$:

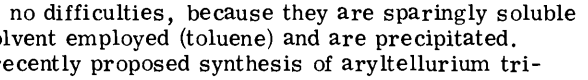
$$(C_6H_5)_3PbCl + TeCl_4 \rightarrow C_6H_5TeCl_3 + (C_6H_5)_2PbCl_2 ; \quad (I.5)$$

$$(C_6H_5)_3SnCl + TeCl_4 \rightarrow C_6H_5TeCl_3 + (C_6H_5)_2SnCl_2 ; \quad (I.6)$$

$$(C_6H_5)_4Sn + TeCl_4 \rightarrow C_6H_5TeCl_3 + (C_6H_5)_3SnCl . \quad (I.7)$$

The reaction of $(C_6H_5)_3PbCl$ with $TeCl_4$ proceeds with virtually quantitative yields. Since $(C_6H_5)_2PbCl_2$ is insoluble in dioxan, this makes it possible to separate it readily from $C_6H_5TeCl_3$. Triphenyltin and tetraphenyllead chlorides also give high yields on reaction with $TeCl_4$. The separation of $C_6H_5TeCl_3$ from organotin compounds presents no difficulties, because they are sparingly soluble in the solvent employed (toluene) and are precipitated.

The recently proposed synthesis of aryltellurium trichlorides from aryltrimethylsilanes is related to these reactions. The compounds $ArTeCl_3$ are obtained in high yields on boiling $ArSi(CH_3)_3$ with $TeCl_4$ in toluene[50]:



(I.8)

(e) Synthesis from Diorganoditellurides

An important method of synthesis of organic tellurium trihalides is based on the interaction of ditellurides with halogens:

$$RTe{-}TeR + 3X_2 \rightarrow 2RTeX_3 ; \quad (I.9)$$

X=Cl, Br, or I.

Sulphuryl or thionyl chloride is used instead of chlorine in the synthesis of tellurium trichlorides.

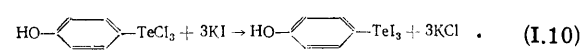
The importance of this method of synthesis consists in the possibility of employing it to obtain aliphatic tellurium trihalides: methyltellurium trichloride[51], tribromide[52], and tri-iodide[53], ethyltellurium tribromide, and tri-iodide[53], and tribromotelluropropionic acid[14]. In the synthesis of aromatic aryltellurium trichlorides this reaction has been used only when the corresponding ditelluride was comparatively readily available. However, the method is perhaps the only convenient procedure for the synthesis of aromatic tellurium tribromides and tri-iodides[14,17,54,55].

In the case of ditellurides the reaction products are as a rule tellurium trihalides, while the reaction of diorganodiselenides with halogens yields mono- and tri-halides depending on the amount of halogen employed. 2-Naphthyltellurium iodide was isolated only in the reaction of di-(2-naphthyl) ditelluride[56]. However, according to some workers[54], aryltellurium monoiodides are obtained together with tri-iodides on treatment of diphenyl and di-*p*-tolyl ditellurides with iodine in solution in carbon tetrachloride at 10–15°C. These relations can apparently be accounted for by the tendency of tri-iodides towards dissociation with liberation of free iodine, which has been noted for arylmethyltellurium di-iodides[55].

The earlier[57] claim that phenyltellurium triacetate can be synthesised by the interaction diphenyl ditelluride with lead tetra-acetate was not confirmed in a more detailed investigation[58].

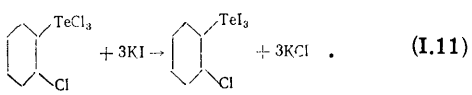
(f) Other Methods of Synthesis

In this section we shall note mainly halogen exchange reactions involving organotellurium trihalides. These reactions have still been comparatively little investigated but nevertheless in certain cases they are of preparative value, particularly when the corresponding ditellurides are not available[57]:



(I.10)

Chlorine is readily exchanged for iodine in 2-chlorocyclohexyltellurium trichloride[38]:



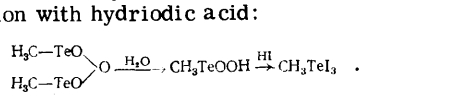
(I.11)

Methyltellurium trifluoride[59] and certain aryltellurium trifluorides[26] have been obtained by the exchange reactions (I.12)–(I.13) with AgF:

$$CH_3TeI_3 + 3AgF \rightarrow CH_3TeF_3 + 3AgI \quad ; \qquad (I.12)$$

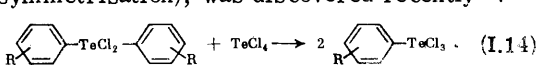
$$ArTeCl_3 + 3AgF \rightarrow ArTeF_3 + 3AgCl \quad . \qquad (I.13)$$

In an early study Drew[60] noted the formation of CH_3TeI_3 from the anhydride of methyltelluric acid on treatment of its aqueous solution with hydriodic acid:



Reactions of this type have been used more frequently to synthesise organoselenium trihalides[61].

The conversion of diaryltellurium dichlorides into aryltellurium trichlorides, based on the reaction of diaryltellurium dichlorides with $TeCl_4$ (a reaction which is the reverse of symmetrisation), was discovered recently[62]:



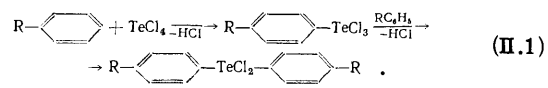
(I.14)

2. METHODS OF SYNTHESIS OF DIORGANO-DERIVATIVES OF TELLURIUM(IV)

(a) Aryltelluration of Aromatic Compounds

If the telluration reaction is carried out in the presence of an excess of an aromatic compound and under conditions more severe than those required to substitute one chlorine atom (a higher temperature), the reaction may proceed further and can lead to diaryltellurium dichlorides.

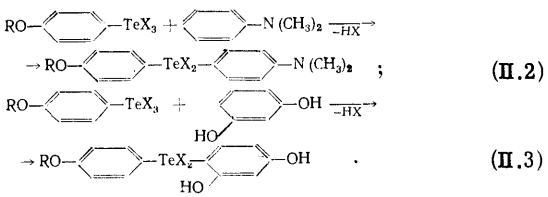
Thus, when $TeCl_4$ is refluxed with a large excess of anisole or phenetole, high yields of di-(*p*-anisyl)tellurium dichloride[13] and di-(*p*-phenetyl)tellurium dichloride[14] are obtained:



(II.1)

The two-stage mechanism of the substitution reaction is demonstrated by the fact that the interaction of *p*-methoxyphenyltellurium trichloride, prepared beforehand, with anisole and of *p*-phenoxyphenyltellurium trichloride with phenyl ether lead to di-(*p*-anisyl) and di-(*p*-phenoxyphenyl)-tellurium dichlorides respectively[16].

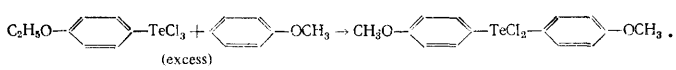
Petragnani[63] used this reaction to synthesise certain asymmetric diaryltellurium dihalides. He established that aryltellurium trichlorides and tribromides (but not tri-iodides) react with dimethylaniline and resorcinol to give aryl-(4-dimethylaminophenyl)- and aryl-(2,4-dihydroxyphenyl)-tellurium dihalides respectively:



(II.2)

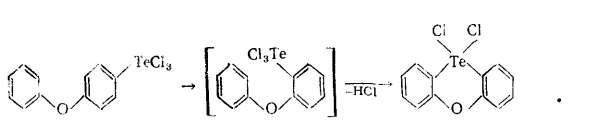
(II.3)

Interesting results were obtained by Bergman[24] in an attempt to reproduce certain earlier studies[13] of the interaction of aryltellurium trichlorides with alkyl aryl ethers. Thus, when *p*-ethoxyphenyltellurium trichloride (1 M) is heated for 6 h with anisole (4 M) at 160°C, only the symmetrical di-(*p*-anisyl)tellurium dichloride is obtained:

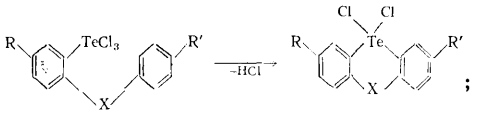


Other compounds of the type $RC_6H_4TeCl_3$ undergo a similar reaction (R = 4-Br or 4-CH_3), but the causes of the exchange of the substituent in the *p*-position relative to the trichlorotelluro-group are still obscure.

If the second aromatic ring attacked by the TeX_3 group is part of the same molecule, intramolecular electrophilic substitution takes place, leading to the formation of heterocyclic tellurium dihalides. Drew[16] observed that heating of *p*-phenoxyphenyltellurium trichloride at a high temperature leads to its conversion into 10,10-dichlorophenoxatellurin, evidently via an intermediate stage in which the *p*-isomer is converted into the *o*-isomer, which could not be isolated:

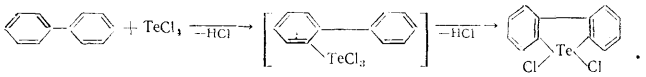


Substituted 10,10-dichlorophenoxatellurins[44,64], and 10,10-dichlorophenothiatellurin[17] were obtained analogously:

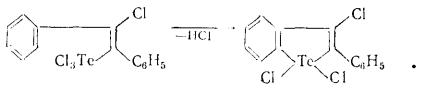


X=O or S.

A similar reaction probably occurs also when tellurium tetrachloride or tetrabromide interacts with biphenyl at a high temperature, the tellurium trichloride formed initially being converted into dichlorodibenzotellurophen[65]:

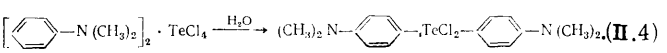


The cyclisation of 2-chloro-1,2-diphenylvinyltellurium trichloride (the product obtained by the addition of $TeCl_4$ to tolan[43]) has been used to synthesise 1,1,3-trichloro-2-phenylbenzotellurophen[66]:



Bergman[24] used the interaction of $TeCl_4$ with an excess of aromatic compounds (benzene, chlorobenzene, and bromobenzene) in the presence of $AlCl_3$ (see Section 1 concerning the role of $AlCl_3$ in the telluration reaction) in order to synthesise certain symmetrical diaryltellurium dichlorides. According to the author, their yields ranged from 30 to 45%.

As stated above, dimethylaniline does not undergo the telluration reaction directly, since its interaction with $TeCl_4$ gives rise to the complex $[PhNMe_2]_2.TeCl_4$, which is converted into di-(*p*-dimethylaminophenyl)tellurium dichloride on heating with water[28]:

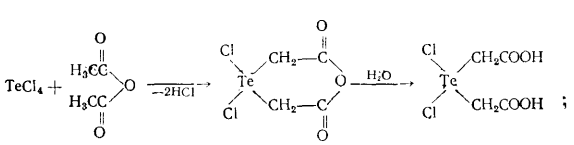


(II.4)

The mechanism of this unexpected reaction has not been studied but the structure of the final product has been clearly demonstrated both by its chemical properties and by ^1H NMR.[67]

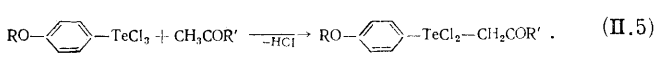
(b) Electrophilic Substitution in Methylenecarbonyl Compounds

If the electrophilic substitution reaction involving aliphatic compounds, considered above, is carried out with compounds containing not one but two activated methyl or methylene groups, then the substitution can occur in both groups. Double substitution is also promoted by an excess of the methyl- or methylene-carbonyl compounds. Thus the interaction of $TeCl_4$ with a large excess of acetic anhydride gives rise to dichlorotellurodiacetic acid (evidently as a result of the hydrolysis of the intermediate anhydride[36]), while the reactions with methyl ketones yield the corresponding diorganotellurium dichlorides[35]:



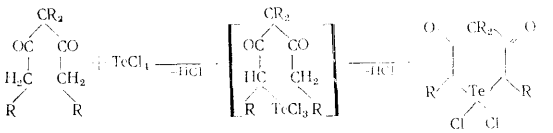
$$TeCl_4 + 2RCOCH_3 \xrightarrow{-2HCl} (RCOCH_2)_2TeCl_2 .$$

In the analogous reactions of aryltellurium trichlorides with acetone and acetophenone the products are respectively acetonyl- and acetophenonyl-aryl tellurium dichlorides[63]:



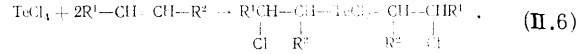
(II.5)

The formation of derivatives of tellurin-3,5-dione by interaction of $TeCl_4$ with β-diketones evidently proceeds via an intermediate organotellurium trichloride, which is converted into a cyclic diorganotellurium dichloride[68-71]:



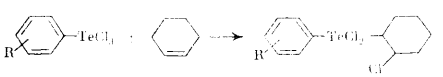
(c) The Addition of $TeCl_4$ and Organotellurium Trichlorides to a Double Bond

The involvement of two olefin molecules in the electrophilic addition of $TeCl_4$ to a double bond leads to diorganotellurium dichlorides. Various workers have shown that, by reacting with an excess of cyclohexene[40,42,72] or ethylene[41,72] in boiling CCl_4, $TeCl_4$ gives rise to addition products:



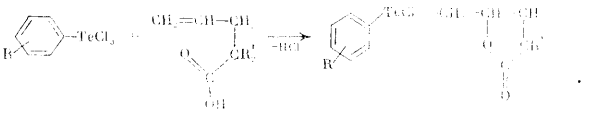
(II.6)

Petragnani[37,38] showed that, like tellurium tetrachloride, certain aryltellurium trichlorides are capable of adding to the double bond of cyclohexene to form aryl-2-chlorocyclohexyltellurium dichlorides:



However, like the reaction of tellurium tetrachloride, this reaction is not general. Unsaturated compounds such as styrene, di-isobutene, and 1,4-diphenylbutadiene are not involved in it and the initial aryltellurium trichlorides are recovered unchanged from the reaction mixture[38].

When aryltellurium trichlorides interact with γ, δ-unsaturated acids, the addition to the double bond is accompanied by cyclisation[37,38,73] with formation of 5-aryldichlorotelluro-2,2-diphenylpentanolactones:



2-Chlorocyclohexyltellurium trichloride undergoes an analogous reaction[38]. The structure of the above dichlorotellurolactone was confirmed by its specific synthesis[38] from an aryltellurium trichloride and 5-chloromercuri-2,2-diphenylpentanolactone, known previously. A study was also made of the interaction of $TeCl_4$ with but-1-ene[40,42], propene[40,41], and butadiene[41], leading to the formation of organotellurium trichlorides and diorganotellurium dichlorides.

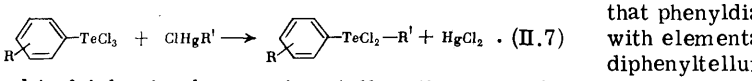
The interaction of 1,1-diarylethylenes with $TeCl_4$ is unusual. The high electrophilicity of the conjugated methylene group in compounds of this type leads to the preferential substitution of a methylene hydrogen atom. When the

reaction was carried out in ether, bis-(1,1-diarylethylene)-tellurium dichlorides were obtained in low yields instead of the products of the addition of $TeCl_4$ to the double bond:

$$(RC_6H_4)_2C{=}CH_2 + TeCl_4 \rightarrow \begin{matrix}(RC_6H_4)_2C{=}CH\\ (RC_6H_4)_2C{=}CH\end{matrix}\!\!>TeCl_2 \quad .$$

(d) Exchange Reactions of Aryltellurium Trihalides and $TeCl_4$ with Organoelemental Compounds

The reaction of aryltellurium trichlorides with aryl(alkyl)-mercury chloride is very important preparatively. Depending on the structure of the initial reactants, it leads to symmetrical or asymmetric diaryltellurium dichlorides[46,75] or alkylaryltellurium dichlorides[75]:



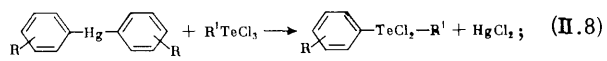
(II.7)

The method is fairly simple experimentally; the best solvent for the reaction is dioxan, which not only dissolves aryltellurium trichlorides effectively but also gives rise to a molecular compound with mercury(II) dichloride, which is precipitated on cooling the reaction mass. The use of aryltellurium tribromides and tri-iodides in this synthesis has not been studied.

In order to obtain symmetrical diaryltellurium dichlorides, it is possible to employ the reaction of arylmercury chlorides with $TeCl_4$ taken in molar proportions of 2 : 1:[2]

$$2ArHgCl + TeCl_4 \rightarrow Ar_2TeCl_2 + 2HgCl_2 \quad .$$

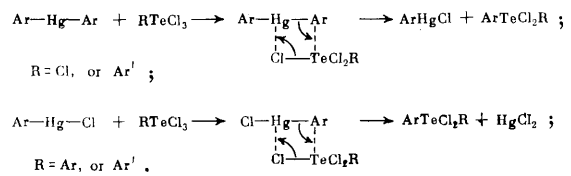
However, in this case diaryltellurium dichlorides are obtained in a less pure form than in the reaction of equivalent amounts of an arylmercury chloride and an aryltellurium trichloride. It has been shown recently that diaryltellurium dichlorides can be obtained in high yields by the reaction of a substituted diarylmercury with tellurium tetrachloride or aryltellurium trichlorides[76]:



(II.8)

R^1 = Cl, or Ar .

According to the view adopted[77], the mechanism of the above reactions involves the formation of a four-centre transition state:



It is of interest to note that the reaction of di-(*p*-nitrophenyl)mercury stops at the first stage: when $TeCl_4$ was introduced into the reaction, *p*-nitrophenylmercury chloride was obtained in 64% yield. This is probably associated with the reduction of the nucleophilic properties of the Mg–Ar bond in *p*-nitrophenylmercury chloride and with the weakening of the electrophilic properties of the trichlorotelluro-group (particularly in *p*-nitrophenyltellurium trichloride) compared with tellurium tetrachloride.

Organolead[48], organotin[49], and organosilicon[50] compounds have also been used to synthesise both symmetrical and asymmetric diaryltellurium dichlorides:

$$Ar_4Pb + TeCl_4 \rightarrow Ar_2TeCl_2 + Ar_2PbCl_2 \quad ; \qquad (II.9)$$

$$Ar_2Pb(CH_3)_2 + TeCl_4 \rightarrow Ar_2TeCl_2 + (CH_3)_2PbCl_2 \quad ; \qquad (II.10)$$

$$Ar_3PbCl + Ar'TeCl_3 \rightarrow ArTeCl_2Ar' + Ar_2PbCl_2 \quad ; \qquad (II.11)$$

$$Ar_4Sn + TeCl_4 \rightarrow Ar_2TeCl_2 + Ar_2SnCl_2 \quad ; \qquad (II.12)$$

$$Ar_3SnCl + Ar'TeCl_3 \rightarrow ArTeCl_2Ar' + Ar_2SnCl_2 \quad ; \qquad (II.13)$$

$$ArSi(CH_3)_3 + Ar'TeCl_3 \rightarrow ArTeCl_2Ar' + (CH_3)_3SiCl \quad . \qquad (II.14)$$

(e) The Diazo-method

The diazo-reaction for the synthesis of organic derivatives of tellurium(IV) was first used by Waters, who showed that phenyldiazonium chloride in acetone reacts on cooling with elemental tellurium, giving rise to a low yield of diphenyltellurium dichloride[78]:

$$2RC_6H_4N_2Cl + Te \rightarrow (RC_6H_4)_2TeCl_2 + 2N_2 \quad . \qquad (II.15)$$

According to Waters' observation, the yield of diphenyltellurium dichloride can be increased somewhat by employing instead of phenyldiazonium chloride its double salt with zinc chloride. Subsequently Tanijama et al.,[79] who used Waters' method, obtained a series of diaryltellurium dichlorides in low yields.

It has been shown that the principal version of Nesmeyanov's diazo-method[27], based on the decomposition of double salts of an arenediazonium chloride with tellurium tetrachloride, having the formula $(ArN_2)_2TeCl_6$,[80-82] under the influence of powdered copper in acetone[83], can be used to synthesise diaryltellurium dichlorides

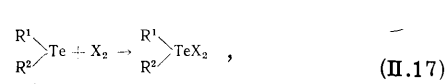
$$(ArN_2)_2TeCl_6 + 4Cu \rightarrow Ar_2TeCl_2 + 2N_2 + 4CuCl \quad . \qquad (II.16)$$

The double salts were obtained in yields of 85–95% on mixing solutions of an arenediazonium chloride and tellurium tetrachloride in concentrated HCl. The yields of diaryltellurium dichlorides are between 20 and 50% depending on the nature of the substituent.

Nesmeyanov et al.[84] proposed another version of the diazo-reaction. Benzenediazonium tetrafluoroborate was treated with zinc dust in acetone solution in the presence of $TeCl_4$. The reaction probably proceeds via diphenyltellurium dichloride and leads directly to diphenyl telluride. The yield of the latter, isolated as diphenyltellurium dibromide, is only 6%.

(f) The Synthesis of Diorganotellurium Dihalides from Other Organotellurium Compounds. The Synthesis from Diorganotellurides and Diorganoditellurides

A widely used method for the synthesis of diorganotellurium dihalides involves the addition of halogens to diorganotellurides:



R^1, R^2 = Ar or Alk; X = Cl, Br, or I. (II.17)

The addition of chlorine, bromine, and iodine proceeds readily under the influence of free halogens in an inert solvent (benzene, CCl_4, and, more rarely, chloroform and ethyl ether) with slight cooling. Thionyl or sulphuryl chlorides are also frequently used to synthesise diorganotellurium dichlorides. The above reactions are used particularly frequently in converting diorganotellurides into

diorganotellurium dibromides and di-iodides[85], since direct introduction of these tellurium-containing functional groups into aromatic and aliphatic fragments is difficult.

The considerable affinity of diorganotellurides for halogens can be used in the synthesis of olefins. Like diaryl ditellurides[86], diaryl tellurides debrominate vicinal dibromides, which leads to the formation of olefins in high yields[87]:

$$ArTeAr' + \underset{Br}{\overset{|}{R}}CH-\underset{Br}{\overset{|}{C}}HR' \rightarrow ArTeBr_2Ar' + RCH=CHR' \quad .$$

Even metal salts can serve as donors of halogens. Thus the following reaction takes place on heating di-(*p*-tolyl)-telluride with certain metal chlorides in glacial acetic acid (sealed tube, 100–140°C)[88]:

$$a\,Ar_2Te + b\,MX_n \rightarrow a\,Ar_2TeX_2 + b\,MX_{n-2} \quad ;$$
$$M=Fe^{3+},\ Cu^{2+},\ \text{or}\ Hg^{2+};\ X=Cl.$$

The interaction of diaryl ditellurides with tellurium tetrahalides[86], aryltellurium trichlorides, and diarylselenium dihalides[86] also leads to diaryltellurium dihalides:

$$2Ar_2Te_2 + TeX_4 \rightarrow 2Ar_2TeX_2 + 3Te\ (X=Cl,\ Br,\ I)\ ;$$
$$2ArTeCl_3 + 2Ar_2'Te_2 \rightarrow 3Ar_2'TeCl_2 + 3Te\ ;$$
$$Ar_2SeBr_2 + Ar_2'Te_2 \rightarrow Ar_2'TeBr_2 + Ar_2Se + Te\ .$$

The study of the kinetics of the exchange of halogen atoms in diaryltelluride–diaryltellurium dihalide systems[89], demonstrated by Nefedov et al.,[90] was begun recently by NMR:

$$Ar_2Te + Ar_2'TeX_2 \rightleftarrows Ar_2TeX_2 + Ar_2'Te\ ;$$
$$X=F,\ \text{or}\ ClBr\ .$$

Di-(*p*-anisyl)- and di-(α-naphthyl)tellurium difluorides have been obtained by treating the corresponding diaryl tellurides with tri-(*p*-tolyl)bismuth difluoride[91,92], but they have been identified only chromatographically.

The conversion of diaryl tellurides into the corresponding difluorides is best achieved by the interaction of diaryl tellurides with SF_4 in boiling benzene[93]:

$$Ar_2Te \xrightarrow{SF_4} Ar_2TeF_2. \qquad (II.18)$$

It is of interest that the same compounds are obtained by the reaction of diaryl ditellurides with SF_4; this involves the elimination of one tellurium atom[93]:

$$Ar_2Te_2 \xrightarrow{SF_4} Ar_2TeF_2 + Te\ . \qquad (II.19)$$

Diorganotellurides can be converted not only into the corresponding dihalides but also into diacyloxy-derivatives with the aid of the addition reaction. Compounds of this type have been obtained by the reaction of dialkyl tellurides with benzoyl peroxide[94,95]:

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!Te + (C_6H_5COO)_2 \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!Te\,(OCOC_6H_5)_2 \qquad (II.20)$$

and by the oxidation of diaryl tellurides with lead tetraacetate[57,58,96]:

$$Ar_2Te + Pb\,(OCOCH_3)_4 \rightarrow Ar_2Te\,(OCOCH_3)_2 + Pb\,(OCOCH_3)_2\ . \qquad (II.21)$$

The most convenient method for the preparation of aliphatic di-iodides is the interaction of tellurium and alkyl iodides[4,97,98]:

$$2RI + Te \rightarrow R_2TeI_2\ . \qquad (II.22)$$

These reactions, which apparently proceed via the dialkyl telluride stage, are carried out over a period of several days on heating in sealed tubes.

Exchange of halogens in diorganotellurium dihalides. Diorganotellurium dibromides and di-iodides can also be obtained by the exchange of chlorine atoms in diorganotellurium dichlorides. For example, di-(*p*-dimethylaminophenyl)tellurium di-iodide can be obtained from the dichloride on treating the latter with an aqueous KI solution[28]:

$$(CH_3)_2N-C_6H_4-TeCl_2-C_6H_4-N(CH_3)_2 + 2KI \xrightarrow[-2KCl]{} (CH_3)_2N-C_6H_4-TeI_2-C_6H_4-N(CH_3)_2\ . \qquad (II.23)$$

and aryl-(*p*-dimethylaminophenyl)tellurium bromides can be synthesised by the reaction of the corresponding dichlorides with hydrobromic acid[63]:

$$R-C_6H_3-TeCl_2-C_6H_3-N(CH_3)_2 \xrightarrow{2\,HBr} R-C_6H_3-TeBr_2-C_6H_3-N(CH_3)_2\ . \qquad (II.24)$$

Similarly the chlorine atoms in (di-2,2-diphenylvinyl)tellurium dichlorides can be readily exchanged for bromine or iodine atoms on treatment with KBr or KI solutions[74]; according to the authors, this can involve the exchange of one or both chlorine atoms:

$$(Ph_2C=CH-)_2TeCl_2 + KX \xrightarrow[-KCl]{KX} (Ph_2C=CH-)_2TeClX \xrightarrow[-KCl]{KX} (Ph_2C=CH-)_2TeX_2$$
$$X=Br,\ \text{or}\ I\ .$$

Di-(2-chloro-2-phenylvinyl)tellurium dichloride also readily exchanges the chlorine atoms attached to the tellurium atom in the reaction with potassium iodide[43]:

$$(C_6H_5CCl=CH-)_2TeCl_2 + 2KI \xrightarrow[-2KCl]{} (C_6H_5CCl=CH-)_2TeI_2\ .$$

The exchange reactions are particularly useful in those cases where the corresponding diorganotellurides are unstable and direct halogenation is therefore impossible. Thus certain arylbenzyltellurium dihalides have been synthesised[75] in accordance with the following scheme:

$$ArTeCl_2CH_2C_6H_5 \xrightarrow[-2KCl]{2KI} ArTeI_2CH_2C_6H_5 \xrightarrow[-AgI]{2AgBr} ArTeBr_2CH_2C_6H_5\ . \qquad (II.25)$$
$$\xrightarrow[-2AgCl]{2AgBr}$$

The same method has been used to synthesise aryl-(2,4-dihydroxyphenyl)tellurium dibromides and di-iodides[63], since aryl-(2,4-dihydroxyphenyl)tellurium dichlorides give rise to the corresponding ditellurides on reduction.

One must also note that diorganotellurium dibromides and di-iodides can be converted into the corresponding dichlorides by treatment with thionyl chloride or chlorine and di-iodides can be converted into dibromides on treatment with bromine or phosphorus tribromide[99].

Halogen atoms are also substituted comparatively readily by fluorine atoms and acyloxy-groups. Thus, treatment of the corresponding dihalides with AgF in a suitable solvent can yield diorganotellurium difluorides[26]:

$$R_2TeX_2 + 2AgF \rightarrow R_2TeF_2 + 2AgX\ ;$$
$$R=Ar,\ \text{or}\ Alk;\ X=Cl,\ \text{or}\ I. \qquad (II.26)$$

On the other hand, when silver salts of carboxylic acids were allowed to react with diaryltellurium dichlorides, the corresponding diaryltellurium diacylates were isolated[88]:

$$Ar_2TeCl_2 + 2AgOCOR \rightarrow Ar_2Te\,(OCOR)_2 + 2AgCl\ . \qquad (II.27)$$

Synthesis from diorganotellurium oxides. The reaction of diorganotellurium oxides with hydrogen halides in an aqueous medium is sometimes also used to

synthesise diorganotellurium dihalides:

$$R_2TeO + 2HX \rightarrow R_2TeX_2 + H_2O \quad ; \qquad \text{(II.28)}$$

R=Ar, or Alk; X=F, Cl, Br, or I.

This reaction is used most frequently in relation to aliphatic compounds, which makes it possible to avoid the synthesis of dialkyl tellurides, which have an extremely unpleasant smell. Thus, when dimethyltellurium di-iodide is acted upon by moist silver oxide, a solution of the hydrated form of dimethyltellurium oxide is formed and its treatment with hydrogen halides results in the formation of dimethyltellurium dihalides [100]. Among aromatic compounds, the interaction of aqueous solutions of diaryltellurium oxides with hydrofluoric acid to form diaryltellurium difluorides is of preparative importance [67].

A general method for the synthesis of diaryltellurium diacylates, based on the interaction of diaryltellurium oxides with carboxylic acid anhydrides was discovered

Table 2. Diorgano-derivatives of tellurium(IV) of the type $R^1R^2TeX_2$.

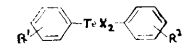
R^1	R^2	X	M.p., °C	Method of preparation	Yield, %	References
Diaryl derivatives of the type 						
H	H	F	154	(II.18), (II.19) (II.26), (II.28)	60—87	93, 59, 67
H	H	Cl	160—161	(II.1), (II.8), (II.13), (II.15)—(II.17)	36, 58, 75—98, 4, 22, 100	24, 25, 76, 48, 49, 78, 83, 132
H	H	Br	198	(II.17)	69	133
H	H	I	235—236	(II.17)	100	132
H	H	CH_3COO	163—164	(II.21), (II.29)	98, 100	57, 102
H	H	$ClCH_2COO$	107—109	(II.29)	100	102
2-CH_3	2-CH_3	Cl	184—185	(II.15), (II.17)	15, 100	79, 132
2-CH_3	2-CH_3	Br	182	(II.17)	100	132
2-CH_3	2-CH_3	I	175	(II.17)	100	132
3-CH_3	3-CH_3	F	118	(II.28)	60	67
3-CH_3	3-CH_3	Cl	128	(II.15), (II.17)	21, 100	79, 2
3-CH_3	3-CH_3	Br	165—166	(II.17)	100	2
3-CH_3	3-CH_3	I	164	(II.17)	100	2
4-CH_3	4-CH_3	F	163	(II.28)	60	67
4-CH_3	4-CH_3	Cl	163	(II.1), (II.8), (II.9) (II.15)—(II.17)	42, 95, 90, 24, 36, 100	24, 76, 48, 79, 83, 132
4-CH_3	4-CH_3	Br	203—204	(II.17)	100	132
4-CH_3	4-CH_3	I	216	(II.17)	100	132
4-CH_3	4-CH_3	CH_3COO	181—182	(II.21), (II.29)	100	57, 102
4-CH_3	4-CH_3	C_3H_7COO	141—142	(II.27), (II.29)	100	88, 102
4-CH_3	4-CH_3	$C_7H_{15}COO$	85—86	(II.27)	—	88
4-CH_3	4-CH_3	$C_{11}H_{23}COO$	66—68	(II.27)	—	88
4-CH_3	4-CH_3	C_6H_5COO	230—231	(II.27), (II.29)	96, 100	88, 102
4-CH_3	4-CH_3	$ClCH_2COO$	163	(II.29)	100	102
2-OCH_3	2-OCH_3	Cl	184—185	(II.15), (II.17)	23, 100	79, 112
2-OCH_3	2-OCH_3	Br	195—196	(II.17)	100	112
2-OCH_3	2-OCH_3	I	199—200	(II.17)	100	112
3-OCH_3	3-OCH_3	Cl	163	(II.15), (II.17)	23, 100	79, 2
3-OCH_3	3-OCH_3	Br	185—186	(II.17)	100	2
3-OCH_3	3-OCH_3	I	167—168	(II.17)	100	2
4-OCH_3	4-OCH_3	F	131	(II.18), (II.19) (II.26), (II.28)	60—92	93, 26, 67
4-OCH_3	4-OCH_3	Cl	182	(II.1), (II.8) (II.15), (II.16)	95, 86 41, 55	14, 76, 79, 83
4-OCH_3	4-OCH_3	Br	198—200	(II.17)	91	79
4-OCH_3	4-OCH_3	CH_3COO	135—136	(II.21), (II.29)	100	57, 102
4-OCH_3	4-OCH_3	C_3H_7COO	128	(II.29)	100	102
4-OCH_3	4-OCH_3	C_6H_5COO	210—211	(II.29)	100	102
4-OCH_3	4-OCH_3	$ClCH_2COO$	160	(II.29)	100	102
4-OCH_3	4-OCH_3	CF_3COO	152	(II.29)	100	102
4-OCH_3	4-OCH_3	CCl_3COO	122—125	(II.29)	100	102
2-OC_2H_5	2-OC_2H_5	Cl	166	(II.15), (II.17)	9, 100	79, 2
2-OC_2H_5	2-OC_2H_5	Br	183—184	(II.17)	100	2
2-OC_2H_5	2-OC_2H_5	I	214—215	(II.17)	100	2
3-OC_2H_5	3-OC_2H_5	Cl	114—115	(II.15)	23	79
4-OC_2H_5	4-OC_2H_5	F	170	(II.26), (II.28)	16, 60	26, 67
4-OC_2H_5	4-OC_2H_5	Cl	110—111	(II.1), (II.15)	88, 15, 100	111
4-OC_2H_5	4-OC_2H_5	Br	127	(II.17)	100	111
4-OC_2H_5	4-OC_2H_5	I	144	(II.17)	100	111
4-OC_2H_5	4-OC_2H_5	CH_3COO	—	(II.21)	100	57
4-OC_2H_5	4-OC_2H_5	Cl	157—158	(II.1)	52	16
4-$N(CH_3)_2$	4-$N(CH_3)_2$	Cl	188—189	(II.4)	33	28
4-$N(CH_3)_2$	4-$N(CH_3)_2$	Br	149—150	(II.23)	94	173
4-$N(CH_3)_2$	4-$N(CH_3)_2$	I	158—159	(II.23)	100	28
4-$N(CH_3)_2$	4-$N(CH_3)_2$	CH_3COO	183—184	(II.29)	100	102
4-$N(CH_3)_2$	4-$N(CH_3)_2$	C_3H_7COO	132—133	(II.29)	100	102
4-$N(CH_3)_2$	4-$N(CH_3)_2$	C_6H_5COO	188,5—189	(II.29)	100	102
4-$N(CH_3)_2$	4-$N(CH_3)_2$	$ClCH_2COO$	167	(II.29)	100	102
3,4-$(OCH_3)_2$	3,4-$(OCH_3)_2$	Cl	155—156	(II.1)	65	24
2,4-$(OCH_3)_2$	2,4-$(OCH_3)_2$	Cl	204—205	(II.1)	63	24
3-CH_3, 4-OCH_3	3-CH_3, 4-OCH_3	Cl	146—147	(II.1)	52	24
2,5-$(CH_3)_2$	2,5-$(CH_3)_2$	Cl	197—198	(II.17)	100	12
2,5-$(CH_3)_2$	2,5-$(CH_3)_2$	Br	189—190	(II.17)	100	12
2,5-$(CH_3)_2$	2,5-$(CH_3)_2$	I	161—162	(II.17)	100	12
2,4-$(CH_3)_2$	2,4-$(CH_3)_2$	Cl	187—188	(II.17)	100	12
2,4-$(CH_3)_2$	2,4-$(CH_3)_2$	I	181—182	(II.17)	100	12
2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	Cl	178—179	(II.17)	100	109
2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	Br	205—206	(II.17)	100	109
2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	I	111	(II.17)	100	109

Table 2 (Cont'd.)

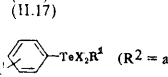
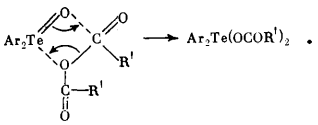
R^1	R^2	X	M.p., °C	Method of preparation	Yield, %	References
2-Cl	2-Cl	Cl	192	(II.15)	33	79
3-Cl	3-Cl	Br	178	(II.17)	95	67
4-Cl	4-Cl	Cl	182—183	(II.15), (II.16)	41, 55	79, 83
4-Cl	4-Cl	Br	184—185	(II.17)	100	2
4-Cl	4-Cl	I	220	(II.17)	100	67
2-Br	2-Br	Cl	244—246	(II.15)	17	79
3-Br	3-Br	Cl	143—144	(II.15)	47	79
3-Br	3-Br	Br	200	(II.17)	95	67
4-Br	4-Br	Cl	190	(II.8), (II.15), (II.1)	90, 40, 44	76, 79, 24
4-Br	4-Br	Br	195—196	(II.17)	90	79
4-Br	4-Br	I	231	(II.17)	90	79
4-F	4-F	Cl	128	(II.17)	95	67
4-F	4-F	Br	171	(II.17)	95	67
2,3,4,5,6-F_5	2,3,4,5,6-F_5	Cl	201	(II.17)	68	132
2,3,4,5,6-F_5	2,3,4,5,6-F_5	Br	210	(II.17)	77	132
2,3-C_4H_4	2,3-C_4H_4	Cl	265	(II.17)	100	108
2,3-C_4H_4	2,3-C_4H_4	Br	244	(II.17)	100	108
2,3-C_4H_4	2,3-C_4H_4	I	184—186	(II.17)	98	2
3,4-C_4H_4	3,4-C_4H_4	Cl	245—246	(II.7), (II.17)	92, 100	46
3,4-C_4H_4	3,4-C_4H_4	Br	253—255	(II.17)	100	46
3,4-C_4H_4	3,4-C_4H_4	I	217—220	(II.17)	94	46
H	4-OCH_3	Cl	114—115	(II.7), (II.8), (II.13), (II.14), (II.17)	87, 97, 80, 30, 100	46, 76, 49, 50, 46
H	4-OCH_3	Br	148.5—149.5	(II.17)	100	46
H	4-OCH_3	I	166—167	(II.17)	100	46
H	4-OC_6H_5	Cl	128.5—129.5	(II.7), (II.17)	70, 100	46
H	4-OC_6H_5	Br	156.5—158	(II.17)	100	46
H	4-OC_6H_5	I	184.5	(II.17)	100	46
H	2,3-C_4H_4	Cl	202.5—203.5	(II.7), (II.17)	80, 100	46
H	2,3-C_4H_4	Br	180.5—182	(II.17)	100	46
H	2,3-C_4H_4	I	212	(II.17)	100	46
H	3,4-C_4H_4	Cl	171.5—172.5	(II.7), (II.17)	76—100	46, 56
H	3,4-C_4H_4	Br	186—187	(II.17)	100	46
H	3,4-C_4H_4	I	182	(II.17)	100	46
4-OCH_3	2,3-C_4H_4	Cl	218—220	(II.7), (II.17)	95, 100	46
4-OCH_3	2,3-C_4H_4	Br	220—222	(II.17)	100	46
4-OCH_3	2,3-C_4H_4	I	189	(II.17)	100	46
4-OCH_3	3,4-C_4H_4	Cl	129.5—130.5	(II.7), (II.17)	84, 100	46
4-OCH_3	3,4-C_4H_4	Br	163—164	(II.17)	100	46
4-OCH_3	3,4-C_4H_4	I	173,5	(II.17)	100	46
4-OC_6H_5	2,3-C_4H_4	Cl	175—176	(II.7), (II.17)	70, 100	46
4-OC_6H_5	2,3-C_4H_4	Br	189—190	(II.17)	100	46
4-OC_6H_5	2,3-C_4H_4	I	184	(II.17)	100	46
4-OC_6H_5	3,4-C_4H_4	Cl	138—139	(II.7), (II.17)	87, 100	46
4-OC_6H_5	3,4-C_4H_4	Br	146—147	(II.17)	100	46
4-OC_6H_5	3,4-C_4H_4	I	206	(II.17)	100	46
2,3-C_4H_4	3,4-C_4H_4	Cl	232—233	(II.7), (II.17)	92, 100	46
2,3-C_4H_4	3,4-C_4H_4	Br	215—217	(II.17)	100	46
2,3-C_4H_4	3,4-C_4H_4	I	205	(II.17)	100	46
4-OC_2H_5	2,3-C_4H_4	Cl	193—194	(II.17)	—	2
4-CH_3	4-CH_3	Cl	158—159	(II.8)	93	76
4-$N(CH_3)_2$	4-CH_3	Cl	170—172	(II.2), (II.24), (II.17)	75—100	63, 173
4-$N(CH_3)_2$	4-CH_3	Br	183—184	(II.2), (II.24), (II.17)	51—100	63, 173
4-$N(CH_3)_2$	4-CH_3	I	130	(II.17)	100, 85	63, 173
4-$N(CH_3)_2$	H	Cl	150—151	(II.17)	95	63, 173
4-$N(CH_3)_2$	H	Br	140	(II.17)	95	63, 173
4-$N(CH_3)_2$	H	I	145—146	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-Br	Cl	151—152	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-Br	Br	168—169	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-Br	I	144—145	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-OC_2H_5	Cl	152—154	(II.2), (II.24), (II.17)	59—100	63, 173
4-$N(CH_3)_2$	4-OC_2H_5	Br	121—123	(II.2), (II.24), (II.17)	49—100	63, 173
4-$N(CH_3)_2$	4-OC_2H_5	I	96—97	(II.17)	100, 94	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	Cl	194—195	(II.2), (II.17)	41, 50	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	Br	188—189	(II.2), (II.24), (II.17)	89—100	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	I	135—136	(II.17)	100, 91	63, 173
4-$N(CH_3)_2$	4-CH_3	Cl	165—166	(II.17)	88	173
4-$N(CH_3)_2$	4-CH_3	I	134	(II.17)	97	173
4-$N(CH_3)_2$	4-Cl	Cl	151—152	(II.17)	86	173
4-$N(CH_3)_2$	4-Cl	Br	146	(II.17)	75	173
4-$N(CH_3)_2$	4-Cl	I	124	(II.17)	82	173
4-$N(CH_3)_2$	3-Br	Cl	149	(II.17)	87	173
4-$N(CH_3)_2$	3-Br	Br	133	(II.17)	84	173
4-$N(CH_3)_2$	3-Br	I	116—118	(II.17)	85	173
4-$N(CH_3)_2$	3-NO_2	Cl	138	(II.7)	50	173
2,4-$(OH)_2$	4-OCH_3	Cl	182—183	(II.3)	70	63
2,4-$(OH)_2$	4-OCH_3	Br	179—180	(II.3), (II.24)	6, 100	63
2,4-$(OH)_2$	4-OCH_3	I	130	(II.24)	100	62
2,4-$(OH)_2$	4-OC_2H_5	Cl	189—190	(II.3)	70	63
2,4-$(OH)_2$	4-OC_2H_5	Br	190—191	(II.3), (II.24)	28, 100	63
2,4-$(OH)_2$	4-OC_2H_5	I	132	(II.24)	100	63
2,4-$(OH)_2$	4-OC_2H_5	Cl	181	(II.3)	61	63
2,4-$(OH)_2$	4-OC_2H_5	Br	181—182	(II.24)	100	62
2,4-$(OH)_2$	4-OC_2H_5	I	122—124	(II.24)	100	63
2,4-$(OCOCH_3)_2$	4-OCH_3	Cl	166—167	(II.3)	88	63
2,4-$(OCOCH_3)_2$	4-OC_2H_5	Cl	162—168	(II.3)	88	63
2,4-$(OCOCH_3)_2$	4-OC_6H_5	Cl	172—173	(II.3)	100	63
4-Br	H	Cl	144	(II.7)	80	67
4-F	H	Cl	132	(II.7)	78	67
4-F	H	Br	177—179	(II.17)	100	67
3-F	H	Cl	150	(II.7)	84	67
3-F	H	Br	184	(II.17)	100	67
			Compounds of the type  (R^2 = alkyl)			
H	CH_3	Cl	157.5—158	(II.17)	86	55
H	CH_3	Br	156.5—157	(II.17)	81	55
H	CH_3	I	146	(II.17)	60—65	55, 85
4-CH_3	CH_3	Cl	150—152	(II.17)	96	55

Table 2 (Cont'd.)

R^1	R^2	X	M.p., °C	Method of preparation	Yield, %	References
4-CH_3	CH_3	Br	163—163.5	(II.17)	75	55
4-CH_3	CH_3	I	135—137	(II.17)	57	55
4-OCH_3	CH_3	Cl	159—160	(II.17)	74	55
4-OCH_3	CH_3	Br	162—163	(II.17)	57	55
4-OCH_3	CH_3	I	115—116	(II.17)	51	55
4-OC_2H_5	CH_3	Cl	142—143.5	(II.17)	81	55
4-Cl	CH_3	Cl	145—146	(II.17)	66	55
4-Cl	CH_3	Br	169—170	(II.17)	80	55
4-Cl	CH_3	I	134—135	(II.17)	72	55
3-Cl	CH_3	Cl	116—117	(II.17)	70	55
4-F	CH_3	Cl	111	(II.17)	100	174
4-F	CH_3	Br	133—134	(II.17)	100	174
4-F	CH_3	I	128	(II.17)	100	174
3-F	CH_3	Cl	94	(II.17)	100	174
3-F	CH_3	Br	137	(II.17)	100	174
3-F	CH_3	I	126	(II.17)	100	174
2-CH_3	CH_3	Cl	95—97	(II.17)	100	182
2-CHO	n-C_4H_9	Cl	105—110	(II.17)	85	182
2-CHO	CH_3	Cl	154—159	(II.17)	100	182
2-$COOC_2H_5$	n-C_4H_9	Cl	135—137	(II.17)	100	182
2-$COOC_2H_5$	CH_3	Br	130—136	(II.17)	100	182
H	C_2H_5	I	96	(II.17)	64	85
H	n-C_3H_7	I	95	(II.17)	62	85
H	iso-C_3H_7	I	97	(II.17)	46	85
H	n-C_4H_9	Br	74—75	(II.17)	95	85
H	n-C_4H_9	I	82—84	(II.17)	84	85
H	n-$C_{14}H_{29}$	I	70	(II.17)	70	85
4-OCH_3	C_2H_5	Cl	80—81	(II.7), (II.17)	30, 100	75
4-OCH_3	C_2H_5	Br	107—108	(II.17)	100	75
4-OCH_3	C_2H_5	I	135	(II.17)	100	75
3,4-C_4H_4	cyclo-C_6H_{11}	Cl	140—141	(II.7), (II.17)	59, 100	75
3,4-C_4H_4	cyclo-C_6H_{11}	Br	157	(II.17)	100	75
3,4-C_4H_4	cyclo-C_6H_{11}	I	139	(II.17)	100	75
4-OCH_3	$C_6H_5CH_2$	Cl	126—127.5	(II.7)	100	75
4-OCH_3	$C_6H_5CH_2$	Br	153	(II.25)	77	75
4-OCH_3	$C_6H_5CH_2$	I	133	(II.25)	75	75
3,4-C_4H_4	$C_6H_5CH_2$	Cl	128.5—130	(II.7)	80	75
3,4-C_4H_4	$C_6H_5CH_2$	Br	149	(II.25)	80	75
3,4-C_4H_4	$C_6H_5CH_2$	I	144	(II.25)	100	75
3,4-C_4H_4	$C_6H_5CH{=}CH$	I	153—154	(II.17)	59	43
3,4-C_4H_4	C_2H_5	Cl	138—139	(II.17)	100	56
3,4-C_4H_4	C_2H_5	Br	141—142	(II.17)	100	56
3,4-C_4H_4	C_2H_5	I	102	(II.17)	100	56
4-OCH_3	CH_2COCH_3	Cl	137—138	(II.5)	65	63
4-OC_2H_5	CH_2COCH_3	Cl	134—135	(II.5)	75	63
4-OCH_3	$CH_2COC_6H_5$	Cl	136—137	(II.5)	60	63
4-OCH_3	$CH_2COC_6H_5$	Br	151—152	(II.5)	29	63
4-OC_2H_5	$CH_2COC_6H_5$	Cl	141—142	(II.5)	57	63
4-OC_6H_5	$CH_2COC_6H_5$	Cl	146—147	(II.5)	46	63
Compounds of the type $R^1TeX_2R^2$ (R^1 and R^2 = alkyl)						
CH_3	CH_3	F	84	(II.26)	—	59
CH_3	CH_3	Cl	92	(II.28)	—	97
CH_3	CH_3	Br	92	(II.28)	—	97
CH_3	CH_3	I	127	(II.22)	50	97
CH_3	CH_3	C_6H_5COO	154	(II.27)	—	97
C_2H_5	C_2H_5	I	57	(II.22)	20	98
n-C_4H_9	n-C_4H_9	I	61	(II.17)	70	94
CH_2CH_2Cl	CH_2CH_2Cl	Cl	111	(II.6)	—	41
$CH_2CHClCH_3$	$CH_2CHClCH_3$	Cl	100	(II.6)	30	41
		Cl	134—135	(II.6)	80	42
n-C_5H_{11}	$CH_2COOC_2H_5$	C_6H_5COO	77—78	(II.20)	—	95
$C_6H_5CCl{=}CH$	$C_6H_5CCl{=}CH$	Cl	205—215	(II.30)	83	43
$C_6H_5CCl{=}CH$	$C_6H_5CCl{=}CH$	I	168—169	(II.17)	100	43
$C_6H_5C{\equiv}C$	$C_6H_5C{\equiv}C$	I	120—125	(II.17)	33	43

recently [101,102]; the reaction probably involves electron transfer via a four-membered transition state:



(II.29)

Synthesis from aryltellurium trichlorides. Apart from the telluration of aromatic and aliphatic systems leading to diorganotellurium dihalides (see above), an unusual method of synthesis of these compounds, involving the symmetrisation of organotellurium trichlorides, will be described in this Section. In certain cases (2-chloro-2-phenylvinyltellurium trichloride) it proceeds fairly readily under the influence of hydroxylated solvents. However, usually such reactions require the use of a symmetrising agent [62]:

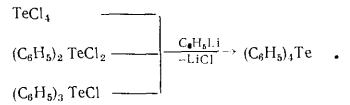
$$2ArTeCl_3 + 4Cu \rightarrow Ar_2TeCl_2 + 4CuCl + Te \ . \qquad \text{(II.30)}$$

Data on diorgano-derivatives of tellurium(IV) are compiled in Table 2.

3. SYNTHESIS OF TETRAORGANOTELLURANES

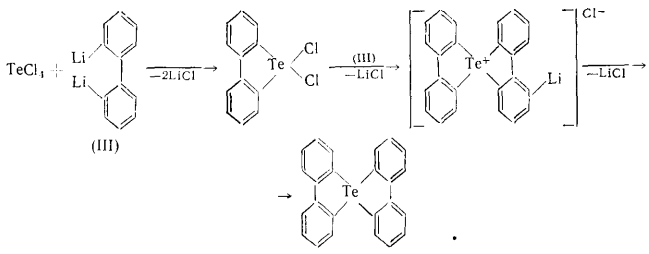
In contrast to tellurium trihalides and dihalides, triorganotellurium halides have an ionic structure in the crystalline state and in solutions [3], i.e. they are telluronium salts and do not therefore belong to telluranes. However, if all four σ bonds are of the Te–C type and are covalent, the corresponding compounds are tetraorganotelluranes.

The synthesis of tetraorganotelluranes is based on the interaction of halogen-containing compounds of tellurium with aryl-lithium derivatives. The first representative of this class (tetraphenyltellurium) has been obtained [103] by the interaction of $TeCl_4$, $(C_6H_5)_2TeCl_2$, or $(C_6H_5)_3TeCl$ with phenyl-lithium:



Tetrakis(pentafluorophenyl)tellurium was obtained similarly [104].

Bis-(2,2-diphenylene)tellurium was synthesised by the reaction of 2,2'-dilithiobiphenyl (III) with $TeCl_4$. [105,106] It is formed via the following mechanism:



This compound was also obtained by the reaction of 2,2'-dilithiobiphenyl with tetra- and hexa-methoxytellurium [105,106].

In order to synthesise tetra-alkyltellurium derivatives, studies were made of the reactions of the corresponding alkyl-lithium derivatives (butyl, methyl) with $TeCl_4$ or trialkyltelluronium iodides [105]. However, tetra-alkyl derivatives of tellurium were never isolated, although their existence in solution as unstable intermediates was postulated on the basis of the study of the composition of the reaction mixture. Other attempts to synthesise tetra-alkyltellurium derivatives [alkyl–aryl exchange between bis(diphenylene)tellurium or triphenyltellurium iodide and butyl-lithium] led to the same results [106].

III. THE SYNTHESIS OF π-TELLURANES

In contrast to σ-telluranes, the methods of synthesis of which have now been developed in fair detail, the synthetic approaches to π-telluranes of different structure have been very little investigated.

1. ATTEMPTS TO PREPARE DIARYLTELLURIUM OXIDES

The commonest method for the synthesis of diaryltellurium oxides is hydrolysis of diaryltellurium dihalides by dilute alkalis or ammonia [107-112]:

$$(RC_6H_4)_2TeX_2 + 2OH^- \rightarrow (RC_6H_4)_2TeO + H_2O + 2X^-;$$

R = H[107-108,110], 4-CH_3[108], 2,3-C_4H_4[111], 2,4,6-$(CH_3)_3$[112], or 4-OC_2H_5[109].

When dialkyl tellurides are oxidised [95] with hydrogen peroxide in an alkaline medium or with nitric acid, the dihydroxide $R_2Te(OH)_2$ and the basic nitrate $R_2TeOH(NO_3)$ are obtained. Complex compounds, for example $R_2TeO.3RTeOOH$, are formed in air or on interaction with other oxidants. On the other hand, when diaryl tellurides are oxidised by nitric acid, the products are the dinitrates $Ar_2Te(NO_3)_2$, whose hydrolysis by alkalis gives rise to diaryltellurium oxides [113].

2. THE SYNTHESIS OF TELLURIUM IMIDES

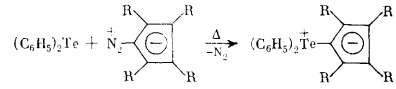
The only method known at the present time for the synthesis of tellurium imides involves the interaction of diaryltellurium oxides with sulphonamides in boiling chloroform [114]:

$$(4\text{-}CH_3OC_6H_4)_2TeO + H_2NSO_2R \rightarrow (4\text{-}CH_3OC_6H_4)_2\overset{+}{T}e-\overline{N}SO_2R;$$

R = 4-$CH_3C_6H_4$, C_6H_5, or $C_6H_5CH_2$.

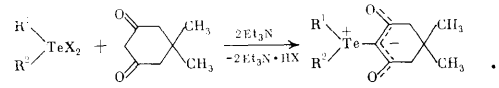
3. THE SYNTHESIS OF TELLURONIUM YLIDS

The methods of synthesis and properties of telluronium ylids have been studied comparatively little. Stable telluronium ylids (cyclopentadienylides) were obtained for the first time [115,116] in the thermal decomposition of the corresponding diazocyclopentadienes in an excess of diphenyl telluride:



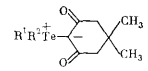
R = H, or C_6H_5.

Later, a large series of dicarbonyl-stabilised telluronium ylids, containing both alkyl and aryl substituents at the tellurium atom, were obtained by a method common to Group VI elements, based on the interaction of diorganotellurium dihalides (chlorides, bromides) with dimedone in the presence of two equivalents of triethylamine [117,118]:



Data for ylids of this type are compiled in Table 3.

Table 3. Diorganotellurium dimedone ylids of the type



R^1	R^2	Yield, %	M.p., °C	μ^*_{exp}, D	μ_{calc}, D	pK_a^{**}
p-$(CH_3)_2NC_6H_4$	*p*-$(CH_3)_2NC_6H_4$	91	149—150	5.49	4.96	11.48
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	89	144	4.16	3.95	10.74
p-$C_2H_5OC_6H_4$	*p*-$C_2H_5OC_6H_4$	97	142—143	4.26	4.09	10.86
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	94	136—137	3.58	3.58	10.69
C_6H_5	C_6H_5	100	158—159	3.16	3.16	10.59
p-BrC_6H_4	*p*-BrC_6H_4	95	156—157	1.74	1.68	10.07
p-FC_6H_4	*p*-FC_6H_4	83	127—128	2.06	1.82	10.22
CH_3	C_6H_5	89	147—148	2.90	—	11.22
CH_3	*p*-$CH_3OC_6H_4$	100	155—156	3.28	—	11.40
CH_3	*p*-$C_2H_5OC_6H_4$	92	96—97	3.42	—	11.25
CH_3	CH_3	80	97—98	3.18	—	12.07
p-$CH_3OC_6H_4$	*p*-$(CH_3)_2CHC_6H_4$	91	103—104	4.06	—	10.69

*In benzene at 30°C.
**In acetonitrile at 25°C.

IV. THE STRUCTURE OF ORGANIC DERIVATIVES OF TELLURIUM (IV)

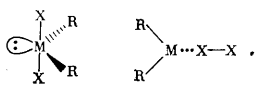
The data accumulated at the present time on the structure of tellurane molecules and their relation with physical and physicochemical properties are at present extremely

limited. In their discussion, it is therefore useful to resort to information about the structure and properties of sulphuranes and selenuranes, which helps to discover certain regularities or tendencies in the structure of tetracoordinate compounds of Group VI elements as a function of the nature of the central atom.

1. THE STERIC STRUCTURE OF σ-TELLURANES

(a) X-Ray Diffraction and Spectroscopic Studies of Molecular Structures

When the halides (X = Cl, Br, or I) react with compounds of the type R_2M (M = S, Se, or Te), there is a possibility, in principle, of the formation of two types of structures: (1) a bisphenoid structure with covalent M–X bonds (IV) and (2) a molecular σ-complex (V):



(IV) (V)

The study of the infrared Raman spectra of the adducts of halogens with R_2M (R = CH_3, M = S, Se, or Te)[119] as well as investigation of the ^1H NMR spectra and electrical conductivities of the products of the interaction of halogens with thiane and selenane[120] led to the conclusion that there is a clear-cut relation between the structure of these adducts and the nature of M and X. Whereas only structure (V) obtains for sulphur derivatives with X = Br or I, for selenium the adducts have structures (IV) with X = Cl or Br and (V) when X = I. For any X, diorganotellurides have the bisphenoid structure (IV) (a trigonal bipyramid) both in the solid phase and in solution, in which the lone electron pair of the tellurium atom plays the role of a third equatorial phantom ligand.

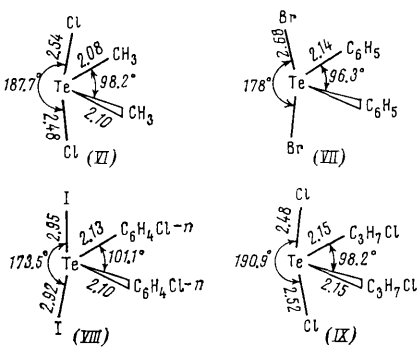


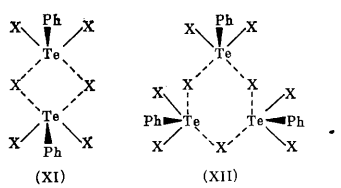
Figure 1. The results of an X-ray diffraction study of dimethyltellurium dichloride (VI)[122], diphenyltellurium dibromide (VII)[123], di-(4-chlorophenyl)tellurium di-iodide (VIII)[124], and di-(2-chloropropyl)tellurium dichloride (IX)[133].

This structure of σ-telluranes with equivalent Te–X bonds (see also data for the NQR spectra of dimethyltellurium dichloride[121] and isotope exchange in the $Ph_2TeCl_2^*$ + Ph_2Te system[90]) has been clearly confirmed by X-ray diffraction studies of dimethyltellurium dichloride (IV)[122], diphenyltellurium dibromide (VII)[123], di-(*p*-chlorophenyl)-tellurium di-iodide (VIII)[124], and di-(2-chloropropyl)tellurium dichloride (IX)[125] (Fig. 1).

Certain data for the Te–C and Te–X bond lengths in the dihalides of a series of tellurium-containing heterocycles have been published[126–131].

On the basis of a comparison of the infrared and Raman spectra of substituted diaryltellurium dihalides of the type R_2TeX_2 (R = *p*-tolyl, *o*-tolyl, *p*-anisyl, or pentafluorophenyl and X = Cl, Br or I) with the spectra of diphenyltellurium dihalides, it has been concluded[132] that in all cases the halogen atoms occupy the axial positions in the trigonal bipyramid.

An X-ray diffraction study has so far been made of only one trihalide—2-chloroethyltellurium trichloride (X)[133,134], obtained by the addition of $TeCl_4$ to ethylene (Fig. 2). Whereas diorganotellurium dihalides are monomeric in the crystal, compound (X) forms in the crystal a polymeric chain with bridge bonds via a chlorine atom. Because of this, the tellurium atom acquires a coordination number of 5 and the chlorine atoms are located at the vertices of a square pyramid. The Te–Cl distance is 2.39 Å and the Te–Cl$_{bridge}$ distance is 2.72 Å. In terms of the Te–Cl bond type, this compound lies between the monomeric dimethyltellurium dichloride[122] and the tetrameric tellurium tetrachloride[135], which is reflected in the average Te–Cl distance (2.39 Å) (2.51 Å in dimethyltellurium dichloride and 2.31 Å in tellurium tetrachloride). Examination of the low-frequency infrared and Raman spectra of various compounds $RTeX_3$ (R = phenyl, *p*-tolyl, *p*-anisyl, *p*-phenetyl, or *p*-phenoxyphenyl; X = Cl, Br, or I) also led to the conclusion that in compounds of this type the tellurium atom is pentacoordinate[54]. According to the authors, the trichlorides and tri-iodides are isomorphous and dimeric in the solid state [structure (XI)], while structure (XII) is quite probable for the tribromides (R = phenyl, *p*-tolyl, or *p*-phenoxyphenyl), which are more associated according to the authors' data. On the other hand, other results[51] showed that the tri-iodide is associated to the greatest extent in the series of methyltellurium trihalides. The structures proposed for the trihalides, based on the donor–acceptor interaction of the $PhTeX_2$ units with bridging halogen atoms, are fairly unstable because aryltellurium trichlorides are monomeric in solution (in dioxan)



(XI) (XII)

The available data suggest that the tendency towards tetracoordination increases appreciably in the sequence S < Se < Te. The influence of the halide ligand on the capacity of the chalcogen for involvement in tetracoordination is appreciable. On passing from F, Cl to Br and I, σ-telluranes are somewhat destabilised. Thus iodotelluranes of the type R_2TeI_2 show a tendency in solutions in polar solvents towards dissociation with a transition from structure (IV) to structure (V).[55] Nevertheless, in the crystalline state the compounds R_2TeI_2 exist as the σ-telluranes (IV). Apart from the X-ray diffraction data for diaryltellurium di-iodides[124], this is indicated by data obtained recently for dimethyltellurium di-iodide[136,137] from ^{125}Te Mössbauer spectra. The parameters of the Mössbauer spectra show clearly that even dimethyltellurium tetrahalides, particularly Me_2TeI_4, are also derivatives of tellurium(IV), i.e. the latter compounds probably have the structure $Me_2TeI_2.I_2$.[137]

(b) The Polarity Rule and the Conformational Effects of Substituents in the Molecules of σ-Telluranes

The above data concerning the molecules of σ-telluranes show that in all the compounds (VI)–(X) the more electronegative substituents occupy the axial positions, which reflects the polarity rule. According to this rule, in polyhedral molecular structures with topologically different bond types, derived from the configuration of a trigonal bipyramid, topomers containing more electronegative substituents in the axial positions exhibit the greatest stability [138–140]. The axial bonds in the corresponding structures are loosened and lengthened by 0.2–0.3 Å compared with the equatorial bonds.

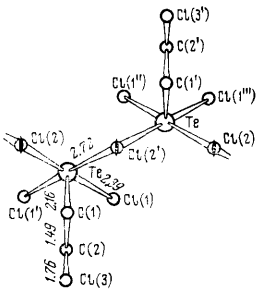


Figure 2. The results of an X-ray diffraction study of 2-chloroethyltellurium trichloride (X) [133].

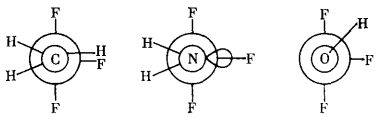
The polarity rule, established initially for phosphoranes, has now received theoretical justification also for tetracoordinate compounds of Group VI elements—sulphuranes and their analogues [141–144]. A clear explanation of the loosening of the diaxial bonds in σ-sulphuranes and their analogues is associated with the structure of the highest occupied molecular orbital, which is regarded, in terms of the perturbation theory, as a combination of a bonding molecular orbital of the angular MR^1R^2 molecule with the antibonding molecular orbital of the extended linear R^3R^4 molecule, where R^3 and R^4 are axial ligands [139,140].

The high stability of configurations in which the most electronegative ligands occupy axial positions is independent of the inclusion in the basis set of the *d* orbitals of the central atom and is determined by the form of the molecular orbital which permits the concentration of electron density at the axial bonds and leads to the accumulation of negative charges at the axial centres.

The fulfillment of the requirements of the polarity rule for σ-telluranes is illustrated, for example, by calculations on the topomers of dibromodichlorotellurium (Fig. 3), which show that tellurane structures with the most electronegative substituents in the axial positions are preferable [144]. In this connection it is interesting to note that, on the basis of Raman spectra, Ozin and Voet [145] initially concluded that $TeCl_2Br_2$ exists in configuration *b* (Fig. 3), but later [146] a more exact calculation led them to attribute conformation *a* to this compound (Fig. 3).

The conformational effects in sulphurane, selenurane, and tellurane molecules, due to the complexity of the dependence of the total energy of the molecule on the rotation of the ligands with lone electron pairs and axial and equatorial π bonds have also been analysed [142,144,147,148]. The general conclusions arising from the theoretical calculations reduce to the following postulates:

1. The introduction of a strong π-acceptor substituent into the molecules of σ-telluranes can stabilise, regardless of the electronegativities of the remaining ligands, its axial conformation in which the axes of the vacant π molecular orbitals of the acceptor and the localised orbital of the lone electron pair are parallel.
2. π-Donor ligands always occupy equatorial positions.
3. In bisphenoid structures of telluranes, as in the systems of analogues located in the highest positions in the Periodic System, the conformational *gauche*-rule holds [149], i.e. the conformation with the greatest number of *gauche*-interactions has the minimum energy. Indeed it follows from calculations [144,147] that the most stable rotational isomeric forms of MF_3R molecules (R = CH_3, NH_2, or OH; M = S, Se or Te) are the conformations (XIII)–(XV).



The above conclusions are so far based exclusively on theoretical calculations and await experimental studies on the new and interesting field of the conformational analysis of tetracoordinate structures of Group VI elements.

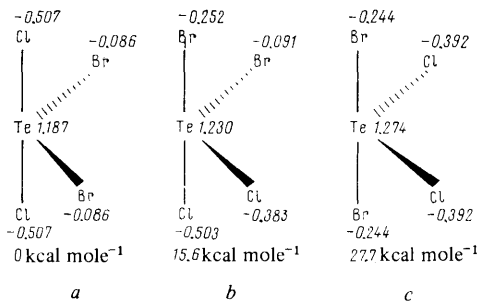
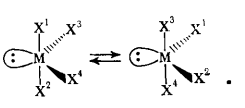


Figure 3. The relative stabilities of various configurations (*a*–*b*) and atomic charges in tellurium dibromide dichloride obtained by the extended Hückel method [144]. (The numerals under the structures indicate their relative energies and those opposite the atoms indicate the atomic charges.)

(c) Polytopic Rearrangements

The stereochemical non-rigidity at the bisphenoid structures of the molecules of σ-sulphuranes and their analogues leads to the possibility of a rapid exchange of the axial (X^1,X^2) and equatorial (X^3,X^4) ligands—topomerisation:



The most convenient method for the investigation of the mechanism and kinetics of such polytopic rearrangements is dynamic NMR. ^{19}F NMR is particularly useful because of the high sensitivity of the ^{19}F nuclei to the characteristics of their chemical environment. The polytopic rearrangements in MF_4 (M = S, Se, or Te) molecules have been investigated [150-154]. It was observed that the topomerisation of SF_4 takes place at a high rate even at room temperature (the separation of the signals of the axial and equatorial fluorine atoms is achieved only at $-98°C$, [150] which corresponds to a barrier of 4.5 ± 0.8 kcal mole^{-1}). For SeF_4, there are only two unresolved peaks even at $-200°C$, which are broadened and merge into a singlet at a temperature $> -190°C$; consequently the exchange in SeF_4 is faster than in SF_4. [150] There is only one sharp peak in the TeF_4 spectrum up to $-100°C$ (the freezing point of the solution). Thus the rate of the axial–equatorial exchange in molecules of the type MF_4 increases in the sequence S < Se < Te. [150]

The rate of ligand exchange is extremely sensitive to the catalytic influence of impurities (H_2O, HF). [154] Indeed, when bis(trimethylsilyl)amine, which binds water, is added to SF_4 solutions, the separation of the signals due to the axial and equatorial fluorine atoms in the ^{19}F NMR spectrum is achieved already at $-60°C$ (this temperature is reproducible, in contrast to earlier studies), which yields an activation energy of 16.3 ± 5 kcal mole^{-1}.

Table 4. The σ constants of tellurium-containing groups.

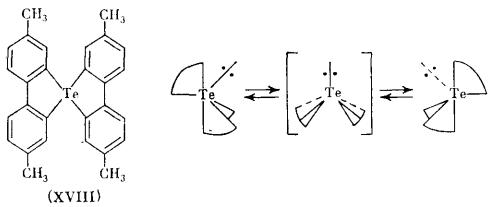
Substituent	δ^F_m, p.p.m.*	δ^F_p, p.p.m.	σ_I	σ_c	σ_n
$Te(CH_3)Cl_2$	−2.93	−4.67	0.50	0.06	0.56
$Te(CH_3)Br_2$	−3.15	−4.86	0.53	0.06	0.59
$Te(CH_3)I_2$	−3.50	−4.79	0.58	0.04	0.62
$Te(C_6H_5)Cl_2$	−3.06	−5.08	0.52	0.07	0.59
$Te(C_6H_5)Br_2$	−3.21	−5.09	0.54	0.06	0.60
$TeCl_3$	−3.28	−6.62	0.55	0.11	0.66
$TeBr_3$	−3.05	−6.43	0.51	0.11	0.62

*The position of the centre of the multiplet relative to the chemical shift of the fluorine signal in fluorobenzene is indicated; the "minus" sign indicates a downfield shift and the "plus" sign indicates an upfield shift relative to δ in C_6H_5F.

The replacement of one of the fluorine atoms by a dialkylamino-group [155,156] or transition to tetra-arylsulphuranes [157] leads to an appreciable decrease of the rate of exchange, which is extremely sensitive to catalytic influences of the impurities. The latter factor indicates a significant role of the intermolecular mechanism of ligand exchange in the polytopic rearrangement (XVI) ⇌ (XVII). Various possibilities of associative, dissociative, and catalytic mechanisms have been examined [158-162]. In dilute solutions and in the gas phase truly intramolecular processes can compete with intermolecular processes [162]. The wide variety of mechanisms of such reactions is still greater than in the series of trigonal bipyramidal structures of Group V elements. Calculations on the pathways followed in the topomerisation of various model sulphuranes, carried out by the CNDO/2 and extended Hückel methods, led to the isolation of two more mechanisms specific to bisphenoid structures: the lever and pyramidal mechanisms, each of which is due to the non-synchronous motion of the ligands involved in the exchange, in contrast to Berry's pseudorotation mechanism [141].

The calculations [141] predict an interesting dependence of the energy to topomerisation in MX_4 molecules via the lever mechanism (the motion of a single axial ligand, while the skeleton made up of the remaining bonds remains stationary). In agreement with experiment, the topomerisation barrier for fluorides decreases on passing from sulphuranes to telluranes. However, for less negative substituents X the situation may be reversed.

In the series of σ-telluranes (except TeF_4) there is yet another experimental indication of a rapid polytopic rearrangement of the type (XVI) ⇌ (XVII). Hellwinkel and Fahrbach [106] explained their observation of the equivalence of all the methyl groups in the spirotellurane (XVIII) as a consequence of Berry's pseudorotation (other mechanisms are hindered by the spiran structure).



(XVIII)

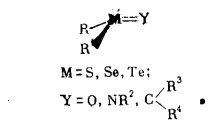
In view of the possible random isochronic nature of the protons of the methyl group (very remote from the chiral centre) the possibility of pseudorotation in structures of type (XVIII) requires further tests.

2. THE STEREOCHEMISTRY OF π-TELLURANES

There are no literature data for the molecular structure of π-telluranes obtained by direct methods. However, it had been concluded earlier on the basis of the results of thermal analysis that the configurations of diaryltellurium and diarylselenium oxides are identical [110].

Like the corresponding sulphonium [163,164] and selenonium ylids [165-167], telluronium ylids should evidently have the structure of a trigonal pyramid with a tellurium atom at the apex. Proof of the high stability of the tellurium pyramid in the dimedone ylids synthesised previously [117] has been obtained [118] by ^1H NMR (using a chiral shift reagent).

Recent theoretical calculations of the inversion and rotational barriers and on the mechanism of the topomerisation of the oxides, ylids, and imides of Group VI elements of type (XIX) [168] revealed definite tendencies in the above series:



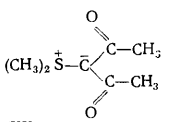
M = S, Se, Te;
Y = O, NR^2, $C\begin{matrix}R^3\\R^4\end{matrix}$.

(XIX)

1. The barriers to the pyramidal inversion of the central atom M in all compounds of type (XIX) with identical Y increase in the sequence S < Se < Te. This justifies the assertion that selenium and tellurium oxides can be resolved into highly stable enantiomers of type (XIX) (M = Te, $R \neq R'$). The methods of synthesis and reactions of these compounds are being studied in detail at the present time [101,102]. Correspondingly, selenium and tellurium imides and ylids with different substituents at the central atom can also exist as stable optically active compounds.

2. The stability of the pyramid of the central atom M and the barrier to pyramidal inversion depend markedly on the nature of Y. In agreement with experimental data, the barrier to inversion in the oxides is highest.

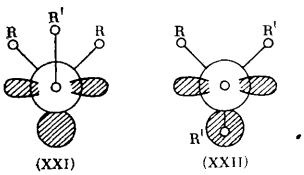
3. On passing from S and Se to Te, the barriers to rotation in the imides and ylids decrease. In the sulphonium ylid of type (XX) (M = S) the barrier to rotation about the C=S bond has been estimated as 12 kcal mole^{-1} [169] on the basis of the broadening of the signals due to the methyl groups in the ^{1}H NMR spectrum on cooling:



(XX)

Such broadening is observed also in the spectra of selenium ylids but at lower temperatures (−60°C),[166] which corresponds to a lowering of the rotation barrier. Presumably in telluronium dimedone ylids the rotation about the Te=C bonds is characterised by particularly high rates.

4. The stable molecular conformation of the imides and ylids of type (XIX) satisfies, according to the calculations, the *gauche*-rule and corresponds to conformation (XXI):



(XXI) (XXII)

This makes it possible to reject conformation (XXII), postulated by Claus and Gycydilik [170] to explain the observed isochronic nature of the signals due to the protons of the methyl groups in aryldimethylsulphimines.

3. THE ELECTRONIC STRUCTURE AND PHYSICAL PROPERTIES OF TELLURANES

(a) The Electronic Effects of Tellurium-Containing Substituents According to Dipole Moment Measurements and ^{19}F NMR

The dipole moments of compounds of the type $RC_6H_4TeX_2C_6H_4R'$ have been determined in a number of studies [67,171-173]. The appreciably higher dipole moments of diphenyltellurium dihalides compared with the corresponding dimethyl derivatives show (taking into account the direction of the C–Te bond moment) that the lone electron pair of the tellurium atom in diphenyltellurium dihalide molecules is not involved in conjugation with the π electrons of the aromatic rings. On the other hand, this difference between the dipole moments can be a consequence of the opposed electronic effect, of which the tellurium atom is capable in principle (d,π conjugation). The inductive and resonance components of the σ constants of the substituents $RTeX_2$ (R = Me or Ph), obtained from the ^{19}F NMR spectra of methyl (and phenyl) derivatives of *p*- (and *m*-)fluorophenyltellurium dihalides [174] with the aid of the Taft equations [175-177] (Table 4), do indeed show that the $RTeX_2$ groups do not exhibit electron-donating mesomeric properties. The σ_C constants of these groups are comparatively small compared with σ_I and, remaining virtually invariant when the halogen is altered, amount to ~ 10% of the overall σ_n constant of the substituent. The σ_I constants increase steadily on passing from chlorine-containing to iodine-containing compounds. Comparison of the values of σ_I and σ_C shows that the above groups interact with the π-electron system of the benzene ring mainly via an inductive mechanism.

When the values of σ_I, σ_C, and σ_n are examined for a series of substituents CH_3TeX_2, it is seen that the increase of the last constant is determined mainly by the increase of the σ_I constant and the values of the σ_n constants of the CH_3TeX_2 groups in the series Cl, Br, I increase on passing from chlorine-containing to iodine-containing compounds. An analogous increase of the σ constants is observed also in the $C_6H_5TeX_2$ series. Here the σ_I constants are greater than for the CH_3TeX_2 groups, evidently owing to the more pronounced inductive properties of the phenyl group compared with the methyl group. Thus one may speak of the preferential inductive mechanism of the interaction of the $RTeX_2$ groups with the π-electron system of the benzene ring. However, as for tellurides [178], when there is an active π-donor substituent (the dimethylamino-group) in the *p*-position relative to the TeX_2 group, there is a possibility of a sharp enhancement of the electron-accepting properties of the tellurium-containing group, probably owing to the population of the vacant *d* orbitals of the Te atom. The experimental dipole moments of aryl(*p*-dimethylaminophenyl)tellurium dihalides greatly exceed the values calculated by the vector scheme [173], the direction of the dipole moment coinciding with the direction expected for d,π conjugation.

In the series of similarly substituted diorganotellurium dihalides the dipole moment increases steadily, like the σ_I and σ_n constants, on passing from the difluorides to the di-iodides. To explain this, it has been suggested [172] that, under the influence of electronegative axial halogen atoms, the lone electron pair of tellurium undergoes contraction to different extents, which leads to a change in the dipole moment and the moment of the molecule as a whole.

A more rigorous explanation in terms of the resolution of the overall moment into the charge and hybridised components [144] was obtained as a result of calculations by the CNDO/2 method with inclusion in the basis set of the *d* orbitals of the central atom of the molecules of dimethylchalcogen dihalides $(CH_3)_2MX_2$. An increase of the dipole moment in the series X = F, Cl, or Br and M = S or Se can be accounted for by the simultaneous increase of the point component and the decrease of the *pd*-hybridised component (the *sp* components remain almost constant).

The problems of the electronic properties of TeX_3 groups have been investigated by ^{1}H and ^{19}F NMR [148,174] and by the dipole moment method [148].

The ^{1}H NMR spectra of *p*-substituted aryltellurium trihalides show that the *o*,*o'*- and *m*,*m'*-protons are isochronous and the barrier to rotation about the Te–Ar bonds is therefore small. The chemical shifts of the *o*-protons of aryltellurium trichlorides, which occur in a very weak field, indicate a strong deshielding effect of the trichlorotelluro-group, whose magnitude (δ_0^H = −1.0 ± 0.1 p.p.m.) is comparable to the analogous effect of the nitro-group. The value of δ_M^H for the $TeCl_3$ group has been calculated from the chemical shifts of the *m*-protons (satisfactorily correlated with the substituent constants δ_0^H),[148] as −0.23 p.p.m., which almost agrees with the corresponding value for the nitro-group. These data agree with the strong negative inductive effect of the $TeCl_3$ group.

The chemical shifts of the *o*-protons of the tribromides and *p*-substituted trichlorides are almost identical and the chemical shifts of *m*-protons are displaced upfield by

0.15–0.25 p.p.m., which indicates a smaller negative inductive effect of the tribromotelluro-group compared with the trichlorotelluro-group.

The σ_C constants of the TeX_3 groups, determined from ^{19}F NMR data [174], amount to 15% of the overall electronic effect of the substituent, which indicates a predominantly inductive nature of the interaction of these substituents with the π-electron system of the ring. In the Cl, Br series, the σ_n constants of the TeX_3 groups diminish, which is consistent with the overall ^1H NMR spectroscopic data.

The dipole moments of aryltellurium trichlorides calculated by the usual vector scheme agree satisfactorily with the experimental values. The vector of the dipole moment of the $TeCl_3$ group, equal to that of the dipole moment of phenyltellurium dichloride, makes an angle of 115° with the Ph–Te bond, which agrees closely with the direction of the equatorial Te–Cl bond. The absence of the moment of the interaction of the $TeCl_3$ group and the nitro-group in the benzene ring indicates the localisation of the lone electron pair and the similar dipole moments of phenyl- and methyl-tellurium trichlorides confirm the absence of an appreciable mesomeric electron-accepting effect of the $TeCl_3$ group.

The results of the calculation of orbital populations and examination of the nature of the highest bonding and lowest vacant molecular orbitals explain the causes of the observed characteristics of the electronic properties of the trichlorotelluro-group. The π-electron system of the benzene ring is only slightly affected by substituent influences and retains six electrons. The large positive charge on the tellurium atom is due to the merging of its p_Z orbital with a combination of suitable orbital symmetry, of the p_X and p_Z orbitals of the chlorine atoms in the π molecular orbital [148].

(b) The Basicity and Dipole Moments of π-Telluranes

The thermodynamic basicity constants of diorganotelluronium dimedone ylids in anhydrous acetonitrile and the correlation of the pK_a values with the σ constants of the substituents have been investigated [118]. Ylids of this type are fairly strong bases (Table 3), comparable in strength with aromatic amines. In the series of dicarbonyl-stabilised ylids of Group VI elements, having structures of the same type, the basicity increases in the sequence S < Se < Te, i.e. increases with decrease of the electronegativity of the 'onium atom and with increase of its size (an analogous relation obtains also for the ylids of Group V elements [179]). The pK_a values of the ylids investigated are best correlated with the σ^0 constants of the substituents ($r = 0.983$; $\rho = 0.958$), which indicates a predominantly inductive effect of the interaction of the aryl rings with the 'onium tellurium atom.

The ylids examined above have relatively low dipole moments compared with the usual values for ylids (Table 3), lying in the range 2–5 D. Such relatively low dipole moments of the ylids, compared, for example, with the dipole moments of diorganosulphonium dicyanomethylides [180] and the fact that they are comparable to the dipole moments of the structurally related arylmethylsulphonium 1,3-indandion ylids (3–5 D) [181] can be explained by the fact that the $Te^+–C^-$ bond moments in telluronium dimedone ylids and the group moment of the dimedone fragment are directed to opposite sides and to a large extent cancel out. In most cases the dipole moments calculated on the basis of a fragmentary vector scheme and determined experimentally agree fairly satisfactorily. The only exception is the *p*-dimethylamino-derivative, where the effect of the direct polar conjugation of the dimethylamino-group with the vacant *d* orbitals of tellurium is evidently manifested.

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During the period when the review was dealt with by the editors a number of new studies were published.

Methods of synthesis of mono-organo-derivatives of tellurium (IV). The interaction of 4-halogeno-substituted diphenyl ethers with tellurium tetrachloride, which proceeds via a stage involving the formation of 2-trichlorotelluro-derivatives and leading ultimately to 10,10-dichlorophenoxatellurins, has been investigated [184,185]. Berry et al. [186] established that, when acetic anhydride reacts with $TeCl_4$, bis(trichlorotelluro)methane is indeed formed and its reduction by potassium metabisulphite yields cyclo-1,4-dimethylenetetratellurium $\overbrace{CH_2–Te_4–CH_2}$. It has been shown [187] that organotin compounds of the type R_3SnBr and R_4Sn react with $TeBr_4$ (there is no reaction with TeI_4 or the yields are extremely low) to form organotellurium tribromides or diorganotellurium dibromides. An earlier report [57] of the synthesis of phenyltellurium triacetate on oxidation of diphenyl ditelluride with lead tetra-acetate was not subsequently confirmed. Although the presence of $C_6H_5Te(OCOCH_3)_3$ in solution was demonstrated by NMR, [188,189] attempts to isolate this compound in a pure form yielded only a substance of unknown structure. Aryltellurenyl halides ArTeX (X = Br or I), obtained by the reaction of diaryl ditellurides with one equivalent of a halogen in non-polar solvents [190,191], are unstable compounds, particularly in the case of bromine, which disproportionates to diaryltellurium dihalides and elemental tellurium [192]. Use of these compounds in the synthesis of asymmetric diaryl tellurides and selenotellurides has been described by Petragnani [193].

Methods of synthesis of diorgano-derivatives of tellurium (IV). Diphenacyl- and arylphenacyl-tellurium dichlorides have been obtained by the reaction of the trimethylsilyl ether of the enolic form of acetophenone with $TeCl_4$ and aryltellurium trichlorides [194]. Symmetrical and asymmetric diaryltellurium dichlorides have been obtained by treating sodium (or potassium) tellurophenoxides with arene-diazonium tetrafluoroborates in ethanol with subsequent chlorination [195] or by the arylation of diaryl ditellurides with arenediazonium chlorides in the presence of copper(II) salts [196]. A new class of diorgano-derivatives of tellurium(IV)—diaryltellurium di-isocyanates $Ar_2Te(NCS)_2$—have been synthesised by the oxidation of diaryl tellurides with free thiocyanogen [197,198] or by the interaction of diaryltellurium dichlorides with ammonium thiocyanate in methanol [198]. A series of studies have been devoted to methods of synthesis and the investigation of the properties of diaryltellurium diacylates. Petragnani [199] obtained these compounds by treating diaryltellurium dichlorides with carboxylic acids in the presence of silver oxide and Pant [189] synthesised them by oxidising diaryl tellurides with lead tetra-acetate and by the double decomposition of diaryltellurium dichlorides with silver salts of carboxylic acids. In order to obtain diaryltellurium diacylates, including derivatives of dicarboxylic acids, Tamagaki et al. [200] used the reaction, described previously by the present authors [100,101], of diaryltellurium oxides with carboxylic acid anhydrides and the acids themselves. It is of interest to note that dicarboxylic acid anhydrides, for example, phthalic anhydride, give rise to

monomeric compounds on reaction with diaryltellurium oxides, while, according to the results of Dance and McWhinnie[201], the reaction of diaryltellurium dichlorides with sodium salts of phthalic acids yield dimeric diaryltellurium diacylates. The infrared spectra of diaryltellurium diacylates, investigated by Pant et al.,[188] indicate the non-equivalence of the carboxylate groups in certain diaryltellurium diacylates, although according to ^{1}H NMR data both the arene rings and the carboxylate groups are completely equivalent[161]. The mass spectra of diaryltellurium diacylates and certain diaryltellurium dichlorides have been investigated[202,203]. The synthesis of previously unknown esters derived from diorganotellurium dioxides $R_2Te(OR')_2$, based on the interaction of dialkyl- or diaryltellurium dihalides with sodium alkoxides, as well as some of their properties have been described[204].

The synthesis of π-telluranes. Diaryltelluronium ylids have been obtained by refluxing diaryltellurium oxides with active methylene compounds (dimedone, indandione, and nitroacetic and malonic esters) in benzene with simultaneous distillation of the water formed[205]. When tellurium tetrahalides TeX_4 (X = F or Cl) interact with hexamethyldisilamides of acetic and arenesulphonic acids, the products are *N*-substituted halogeno-derivatives of iminotelluryls and tellurium *N*,*N'*-diacyldi-imides[206].

The structure of organic derivatives of tellurium(IV). Crystallographic data have been obtained recently for the compounds *o*-$HCOC_6H_4TeX$ (X = Cl, Br, or I)[207] and a complete X-ray diffraction analysis of di-(*p*-anisyl)telluronium dimedone ylid was carried out[208]. The electronic effects of the tellurium-containing substituents $-Te(CH_3)F_2$, $-Te(C_6H_5)(NCS)_2$, and $-Te(C_6H_5)F_2$ have been investigated[209] with the aid of ^{19}F NMR. Studies have been made on the Mössbauer[210-213] and ^{125}Te NMR[214] spectra of various organotellurium compounds, including σ-telluranes.

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The Stability of Colloid Systems (Theoretical Aspects)

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After a brief description of the development of ideas concerning the nature of the stability of colloids, the main factors (ionic-electrostatic and molecular forces) whose balance determines the resistance of colloids to aggregation, are examined. An account is given of calculations of the free energy of charged particles in an electrolyte solution. The influence of the dense layer of adsorbed ions on the stability of colloids is discussed. The phase transitions in colloid systems, particularly coacervation and the formation of periodic colloid structures, are considered. The problem of thermodynamically stable colloid systems is analysed in connection with the properties of micellar solutions. A brief description is given of the problem of the stability of liquid layers and of the phenomenon of heterocoagulation.
The bibliography includes 281 references.

CONTENTS

I. Introduction 363
II. Ionic-electrostatic and molecular forces of the interaction between colloid particles 365
III. The free energy of charged particles in an electrolyte solution 368
IV. Allowance for monolayer adsorption 374
V. The reversible nature of long-range aggregation 375
VI. Langmuir's thermodynamic concept of coacervation and coagulation processes 377
VII. The formation and stability of periodic colloidal structures 378
VIII. Micellar solutions 380
IX. The formation and stability of liquid films 381
X. Interaction of non-identical surfaces 383
XI. Conclusion 383

I. INTRODUCTION

Colloidal systems or colloids became the object of systematic study in the middle of the XIXth century. At that time they were considered as ordinary solutions of special glue-like substances—hence the origin of the term "colloidal solution". Only when the fundamental differences between colloid systems and glue solutions became understood, the science of colloids was established as an independent discipline. Traditionally it is still referred to as colloid chemistry, because of the earlier view that all the differences between colloidal and normal solutions are determined by the nature of "colloidal substances" and also because studies on such systems have been made mainly by chemists. However, in the course of development of the relevant research, the differences between normal and colloidal solutions were discovered and began to be investigated. These differences are largely physical and sometimes physicochemical. It is not fortuitous that the most important work in the study of colloid systems has been carried out by physicists: Helmholtz, Einstein, de Boer, Langmuir, Gibbs, Bernal, Onsager, Kirkwood, Rayleigh, Perrin, Smoluchowski, Gouy, Chapman, Debye, and others. The traditional term "colloid chemistry" has therefore now become, in essence, obsolete and the term "colloid science" is being increasingly used.

The principal difference between colloid systems and glue solutions is that the kinetic units in the former (colloid particles) consist in the general case of a large fairly indefinite number of molecules, and exhibit to a first approximation the properties of a phase separated from the adjoining phase (dispersion medium) by a very large interface. Hence the enormous role of surface phenomena at the boundary between particles of the disperse phase and the dispersion medium becomes understandable: the formation of an ionic double layer and ion exchange, electrokinetic phenomena, and adsorption. Without the consideration of the role of surface phenomena, the science of colloids would have been completely without theoretical foundation†. A distinction is frequently drawn between colloid and coarsely disperse systems: suspensions and emulsion. However, this difference is extremely arbitrary and depends on the particle size or on the area of interface and is largely qualitative.

All the foregoing considerations make it possible to define colloid science as the physical chemistry of disperse systems or systems with a large interface indissolubly linked to the physical chemistry of surface phenomena. In contrast to the science of solutions, the fundamental problem in this science is that of stability. Its importance is determined by the fact that colloid systems are in the main not in a state of thermodynamic equilibrium and an adequate stability of the colloid system constitutes a condition for its existence as such.

In contrast to solutions, the state of a colloid system can change in two significantly different ways—either by the dissolution of some particles and the growth of others, which are relatively more stable, or by the sticking together but not coalescence of the "primary" particles and the formation of aggregates with or without layers of the dispersion medium between the particle. A condition for equilibrium in a colloid system with respect to processes of the first type, i.e. the condition for the stability (constancy) of the composition of the disperse phase, is minimum free energy of the system relative to the distribution of particles with respect to size—the condition for thermodynamic equilibrium.

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†The role of surface phenomena in colloid science is indicated by the names of the international journals and semiperiodical publications as well as institutes: Journal of Colloid and Interface Science; Advances in Colloid and Interface Science; Institute of Colloid and Interface Science (USA); Surface and Colloid Science (Edited by E. Matijević).

The condition for equilibrium in the system relative to processes of the second type (stability in relation to aggregation) requires the existence of repulsion forces between particles approaching each other, which are capable of interfering with their cohesion under the influence of molecular attraction forces. A general condition for thermodynamic equilibrium may not in fact be fulfilled in this case. A characteristic of stability towards aggregation or of aggregation equilibrium in the system is constancy of the distribution of aggregates with respect to the number of "primary" particles in them. In the simplest case equilibrium can correspond to the absence of aggregates.

In mists and "unprotected" emulsions unhindered cohesion of particles may or may not be accompanied by coalescence. In the former case one should speak of the breakdown of the stability of the composition of the dispersion medium and not of stability with respect to aggregation.

The condition for the thermodynamic equilibrium of particles surrounded by electrical double layers was examined for the first time by March[1]. However, we incorrectly formulated the problem of thermodynamic equilibrium in relation to the changes in the degree of dispersion without the breakdown of monodispersity, i.e. with retention of identical surface curvatures by all the particles. Furthermore, when account is taken of the influence of the difference between the curvatures of the particles on their chemical potential, such a state (at any rate for particles containing one component soluble in the dispersion medium) is labile. On the other hand, it is pointless to consider the possibility or impossibility of a process in which such lability is maintained. This is entirely equivalent to considering from the standpoint of thermodynamics the possibility of the rolling of a sphere along a tightrope. A second error in March's work was failure to understand that the main thermodynamic condition which he considered has a bearing solely on the stability of the composition of the disperse phase and not on stability with respect to aggregation.

When the general condition for thermodynamic equilibrium in relation to changes in the composition of the disperse phase of the system holds, the possibility of the formation of aggregates whose particles are separated from one another by thin layers of the dispersion medium is not ruled out. However, whether this possibility does arise and, if it does, the state of the system (metastable, stable, or labile) are problems which must be solved for each specific case by a more detailed examination.

Thus it is necessary to distinguish two specific forms of stability of colloid systems, which are absent in glue solutions: the stability of the composition of the disperse phase and the stability of the aggregate composition or stability with respect to aggregation. Naturally if aggregation is accompanied by the coalescence of particles, then instability with respect to aggregation entails the instability of the composition of the disperse phase. The existence of two types of stability of colloid systems is one of the manifestations of the fundamental qualitative difference between them and true solutions for which the concept of the stability of the composition of the disperse phase and of stability with respect to aggregation lack significance. At the same time it is possible to consider also a third type of stability, which is common to true solutions and colloids. This is the stability with respect to the separation of the system into two phases or, in the case of colloids, quasi-phases, which differ in the concentrations of the kinetic units—molecules or colloidal particles—and also, possibly, in their distribution‡.

In the present review attention is concentrated on the stability with respect to aggregation, the changes in which are usually faster than the changes in the composition of the disperse phase and are therefore of practical importance. The nature of the stability of the aggregate composition is also important. If the condition of the constancy of the composition of the disperse phase does not hold but varies extremely slowly, the constancy of the composition of the aggregate may be referred to as partial equilibrium, since only some of the conditions for equilibrium are then maintained. Aggregation equilibrium can in this case be only temporary and will inevitably change as the composition of the disperse phase changes in direct functional relation to the latter. An exception is provided by a system where there are no aggregates owing to the operation of strong repulsion forces. Equilibrium in such systems can be maintained also during the variation of the disperse phase composition, at least until the size of the particles approaches molecular dimensions, which makes it easier for them to overcome the repulsion forces arising from other particles. At any rate aggregation stability can be considered independently of the possible instability of the disperse phase composition, ignoring the changes in the latter, provided that they are sufficiently slow.

With this stipulation, the aggregation stability can be of two kinds. Firstly it can be due to the slowness of the coagulation process (or the slowness of the decomposition of aggregates) and its nature is then purely kinetic. The aggregation quasi-equilibrium can be referred to in this instance as the relaxation of frozen or hindered non-equilibrium states (but not metastable equilibria). Secondly, a rigorous constancy of the aggregate composition can obtain when aggregation processes are balanced by the opposed deaggregation processes. As will be shown below (Section V), equilibria of this kind can break down also in consequence of the formation of larger aggregates; in this case one can speak of a metastable equilibrium.

Critical emulsions and micellar solutions (see Section VIII), which are colloid systems in complete thermodynamic equilibrium where the conditions of a constant disperse phase composition and the absence of aggregates are maintained, must be treated as a special case.

Equilibrium periodic colloid structures, formed, for example, by the tobacco mosaic virus or by spherical latex particles, merit a special discussion. This will be done later (see Section VII), where the problem of equilibria in colloid systems of the type of phase equilibria in the usual solutions is considered.

The foregoing considerations are based on the most general postulates and are used merely to throw light on the problem of the concept of stability of colloid systems. It is, however, impossible to reach fairly concrete conclusions about the nature of stability and its characteristics, solely on the basis of general considerations of this kind; concrete conclusions make it necessary to specify in greater detail the physical formulation of the problem, perhaps even at the expense of abandoning the generality of the conclusions. Colloid science entered this fruitful

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‡In considering the different types of stability of colloid systems, we are not concerned with kinetic or sedimentation stability, which is manifested by the presence of a sedimentation-diffusion equilibrium in the system.

path about forty years ago, which led to the development and general recognition and application of the physical theory of the stability of lyophobic colloids.

II. IONIC-ELECTROSTATIC AND MOLECULAR FORCES OF THE INTERACTION BETWEEN COLLOID PARTICLES

We shall now describe briefly the path traversed by colloid science and shall consider the factors which are either little known or have been incorrectly described in many monographs and articles to the detriment of the priority due to Soviet scientists§.

The sensitivity of many colloid systems, for example, metal sols, to electrolytes was noted a long time ago[2-5]. The concentrations of electrolytes for coagulating such systems are low, and decrease sharply with the increasing charge of the counterion[6-8]. Colloid systems of this class have been called lyophobic or electrocratic. Colloid systems which coagulate only at high electrolyte concentrations (of the order of several units on the molar scale), which depend little on the type of counterions, have been assigned to another class. A considerable proportion of such systems, referred to as lyophobic colloids, proved subsequently to be true solutions of polymers, whose particles (macromolecules) do not form an interace with the solvent. They ceased to be classified as colloid systems, because a fundamental feature of the latter is the existence of an interface. However, there remained many colloid systems, which, while not true solutions, are nevertheless fairly stable towards electrolytes. It must be emphasised that the same colloid may lose or acquire sensitivity to electrolytes depending on the state of the surface of its particles, which is determined by the absorption of surface-active molecules or ions[9,10]. It is therefore perhaps more correct to speak of the lyophobic or lyophilic state of colloid systems rather than lyophobic and lyophilic colloid systems. There also exist colloid systems, for example polysilicic acid hydrosols, which do not contain surface-active molecules or ions, and are at the same time relatively insensitive to electrolytes.

It was noted long ago that the stability of lyophobic colloids is as a rule correlated with the electrophoretic mobility of the particles, indicating their charge[11-15]. In considering the repulsion forces between charged particles as the cause of their aggregation stability, some workers attempted, following Freundlich[16], to explain the action of electrolytes by a decrease of the charge under the influence of the adsorption of ions of opposite sign. Together with this idea, Kruyt introduced the hypothesis of solvation as the second stability factor[17,18], apart from the charge, which explains the properties of lyophilic colloids. All these ideas, which remained largely qualitative, were completely inadequate for the creation of a full fledged theory of the stability of colloids with clearly formulated physical principles.

A breakthrough for this problem occurred when, firstly, a narrower problem was formulated: the elucidation of the mechanism of the stability and coagulation of lyophobic systems and, secondly, when the balance between molecular attraction and electrostatic repulsion forces between particles was adopted as a basis. In a qualitative form these forces, considered as responsible for the stability of lyophobic colloids, were examined by Kallmann and Willstatter[19]. The attempt to proceed to a quantitative allowance for such forces is due to Hamaker[21,22]. The latter (and independently de Boer[20]) summarised the London expressions for the energy of the pair interaction between all the molecules of two plates or spheres, as well as the dispersion medium, and found an expression for the energy of the molecular interaction between colloid systems as a function of their radii and the thickness of the layer separating them. However, Hamaker's calculations did not lead to the establishment of a theory of stability, because his empirical formula[23-25] for the energy of electrostatic repulsion was not subsequently confirmed theoretically.

A theoretically well founded method for the calculation of the force and energy of the interaction between colloid species, which depends on the overlap of their diffuse ionic atmospheres, is due to the author of the present review[26-29]. He based the calculation on the expression for the ponderomotive pressure P applied to a unit area of the surface of the colloid particle:

$$P = -\frac{\varepsilon}{8\pi} E^2 + p = -\frac{\varepsilon}{8\pi} |\operatorname{grad}\varphi|^2 + p, \qquad (1)$$

where ϵ is the dielectric constant, φ the electric potential, E the projection of the electric field strength vector at the surface of the particle on to the normal to the latter, and p the hydrostatic pressure at the surface in excess of the hydrostatic pressure in the region where there is no electric field¶. The pressure p at any place satisfies the equation for hydrostatic equilibrium taking into account the electric force acting on the space charge (allowance for the polarisation of the medium causes little change in the final results):

$$\operatorname{grad} p + \rho \operatorname{grad}\varphi = 0. \qquad (2)$$

According to the Boltzmann equation, the concentration of ions and hence the space charge density ρ are a function of the local potential φ:

$$\rho = \rho(\varphi). \qquad (3)$$

Therefore it follows from Eqn. (2) that

$$p = A - \int_0^{\varphi} \rho \, d\varphi, \qquad (4)$$

where the integration constant A is independent of the coordinates and is zero according to the definition of p. When a potential $\varphi = \varphi_0$ has been specified on the surface of the particles, it is the same at all sections of the surface, both internal and external. The force balancing the hydrostatic pressure on each particle is therefore zero regardless of the shape of the latter and the force balancing the ponderomotive forces is determined by the summation of the vector-Maxwell tensions $(\epsilon/8\pi)E^2 = f'$ applied to different sections of the surface. The Maxwell tension f' must be supplemented by the electrostriction number f'':

$$f'' = \frac{1}{8\pi} E^2 \frac{\partial \varepsilon}{\partial \rho} \rho. \qquad (5)$$

However, it is known from electrostatics[32] that this addition does not alter the total ponderomotive force acting on bodies immersed in a liquid or gaseous medium. The explanation is that the electrostriction terms should be

§ For example, in the well known book[85] edited by Kruyt.

¶ Langmuir[30] called this excess pressure the excess osmotic pressure. Verwey and Overbeek[31] point out that it is more rational to call it the excess hydrostatic pressure, with which one must agree.

introduced at the same time into Eqn. (2) and should cause a change in the electrostatic pressure p, acting in the vicinity of the surface, such that it compensates exactly the Maxwell tension. This demonstrates the gross error of Babchin's work [33], where an attempt was made to alter the principles of the theory of the stability of lyophobic colloids by introducing electrostriction terms. This work has been criticised by the present author [34,35] and by Levin [36].

If the surface charge densities have not been specified, the values of E at various sections of the surface of the particles must be determined (for a symmetrical electrolyte) by integrating the Poisson–Boltzmann equation:

$$\frac{4\pi}{\varepsilon}\rho = \Delta\varphi = a \operatorname{sh} \alpha\varphi, \tag{6}$$

where

$$a = \frac{8\pi}{\varepsilon} zec, \tag{7}$$

$$\alpha = \frac{ze}{kT}, \tag{8}$$

Here e is the electronic charge, c the electrolyte concentration (in equiv. cm^{-3}) outside the limits of the ionic double layers, k the Boltzmann constant, T the absolute temperature, z the ionic charge, and Δ the Laplace operator, indicating that the sum of the second derivatives of φ with respect to coordinates is considered:

$$\Delta\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2}.$$

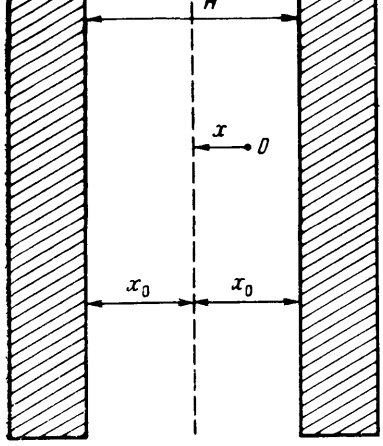


Figure 1. The distribution of potential in the electrolyte layer.

In this general formulation the calculation of the ionic-electrostatic interaction forces between the particles presents enormous mathematical difficulties even for two identical spherical particles.

The present author [26–29] examined initially the simpler case of the interaction of two parallel plates, whose dimensions are so much greater than the gap H separating them that the edge effects may be neglected (Fig. 1). The treatment was restricted initially to the case of low potentials satisfying the condition

$$\frac{ze\varphi}{kT} \ll 1. \tag{9}$$

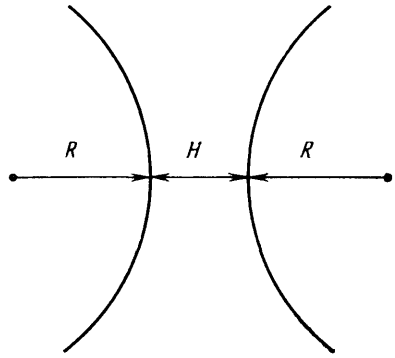


Figure 2. The interaction of two equal spheres.

In this case Eqn. (6) can be written approximately in the form

$$\Delta\varphi = \varkappa^2\varphi, \tag{10}$$

where κ is the reciprocal of the effective thickness d of ionic atmospheres and is given by

$$\varkappa = \frac{1}{d} = \sqrt{a\alpha} = \sqrt{\frac{8\pi}{\varepsilon}\frac{e^2z^2c}{kT}}. \tag{11}$$

In the general case of an arbitrary ionic composition cz^2 must be replaced by the ionic strength $\frac{1}{2}\Sigma z_i^2 c_i$, where c_i is the concentration (in gram-ion cm^{-3}) of the ions having the charge z_i. In the integration of Eqn. (10) it was assumed that a constant potential φ is maintained on the surfaces of the plates regardless of the thickness of the electrolyte layer H:

$$\varphi = \varphi_0, \tag{12}$$

The distribution of the potential between the plates has the following form:

$$\varphi = \varphi_0 \frac{\cosh \varkappa x}{\cosh \varkappa x_0}, \tag{13}$$

where x is the distance from the symmetry plane within the intervening layer to the zero point, where the potential has the required value φ, and $x_0 = H/2$.

Outside the plate, the distribution of the potential is

$$\varphi = \varphi_0 e^{-\varkappa x'}, \tag{14}$$

where x' is the distance from the outer surfaces of the plates. It follows from Eqns. (1), (13), and (14) that the Maxwell tension acting on sections of the inner surfaces of the plates is

$$f_t = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2 \tanh^2 \varkappa x_0, \tag{15}$$

while that on the sections of the outer surface is

$$f_0 = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2. \quad (16)$$

The difference between these tensions is directed to the outside and is equal, according to the foregoing considerations, to the repulsion force N between the plates per unit area:

$$f_0 - f_l = N = \frac{\varepsilon}{8\pi}\varkappa^2\varphi_0^2 \cdot \frac{1}{\cosh^2 \varkappa x_0}. \quad (17)$$

Integration of both parts of Eqn. (17) with respect to x_0 can yield the energy of the interaction between the plates per unit area:

$$U_e = \frac{\varepsilon}{4\pi}\varkappa\varphi_0^2\left[1 - \tanh\left(\varkappa\frac{H}{2}\right)\right]. \quad (18)$$

When applied to the one-dimensional case under consideration, Eqn. (2) becomes

$$\frac{dp}{dx} + \rho\frac{d\varphi}{dx} = 0. \quad (19)$$

Having replaced ρ by $-(\epsilon/4\pi)(d^2\varphi/dx^2)$ and having integrated Eqn. (19), we obtain

$$p = \frac{\varepsilon}{8\pi}E^2 + C, \quad (20)$$

where C is the integration constant.

According to Eqn. (1), the repulsion pressure can be calculated, even if the potential of the surface of the plate changes when the two plates approach one another, by considering the differences between the constants C corresponding to the region between the plates and to the region outside, where $C = 0$. It is therefore sufficient to find the difference between the values of C for the region between the two plates. It is simplest to consider a point in the symmetry plane between the plates where $E = 0$. Then

$$N \equiv C = p_m = -\int_0^{\varphi_m}\rho\, d\varphi, \quad (21)$$

where φ_m is the potential in the symmetry plane.

Thus the force of repulsion between the plates (the "wedging" pressure of the layer between them) is equal to the excess hydrostatic pressure in the symmetry plane. On substituting in Eqn. (21) the expression found with the aid of the Poisson–Boltzmann equation [Eqn. (6)] instead of $\rho(\varphi)$, we find that p_m is equal to the excess osmotic pressure of the ions if it is assumed that the van't Hoff law applies (without the Debye–Hückel correction). In the analogous case of wetting films this led Langmuir to identify N with the excess osmotic pressure of ions at points where $E = 0$. However, as stated before, this is in essence incorrect, because formula (21) is essentially equal to the excess osmotic pressure only for extremely low electrolyte concentrations.

However, for identically charged surfaces, the wedging pressure can be expressed in terms of the potential φ_m, which has many mathematical advantages. The extension of Eqn. (21) to the interaction of spherical particles with the same absolute charges, but different signs of the latter, will be described below.

The transition from the interaction of planar particles to the interaction of spherical particles has been achieved[26–29] with the aid of the transformation proposed earlier by the present author[37]:

$$K = GU(H), \quad (22)$$

where K is an interaction force of any kind (belonging to the class of conservative forces) between convex surfaces, whose radii of curvature are much greater than the effective radii of action of the force (in the present instance twice the thicknesses of the ionic double layers), G a geometrical factor which depends on the radii of curvature of the normal sections of the surfaces near the region of the mutual approach of the particles, and U the energy of the interaction of planar surfaces of the same kind, separated by a plane-parallel layer of the same medium having a thickness H equal to the shortest distance between the convex surfaces under consideration (Fig. 2).

In the simplest case of two identical spheres with a radius R we have

$$G = \pi R. \quad (23)$$

Here it follows from Eqns. (15), (16), and (18) that

$$K = \frac{\varepsilon}{4}R\varkappa\varphi_0^2\left[1 - \tanh\left(\varkappa\frac{H}{2}\right)\right]. \quad (24)$$

Hence integrations with respect to H yields an expression for the energy of the interaction of spherical particles:

$$U(H) = \int_H^\infty K\, dH = \frac{\varepsilon}{2}R\varphi_0^2\ln(1 + e^{-\varkappa H}). \quad (25)$$

In order to estimate the extent to which the calculated repulsion is capable of stabilising the colloid, the present author used the formula for the rate of slow coagulation derived by Fuchs[38] in order to take into account the influence of charges on the rate of coagulation of aerosols:

$$\nu = \frac{4\pi Dc^2}{\int_0^\infty \left[e^{\frac{U(H)}{kT}}/(2R + H)^2\right]dH}, \quad (26)$$

where ν is the number of aggregation steps per unit volume per unit time, D the coefficient of Brownian diffusion of the colloid particles, and c their numerical concentration. In the derivation of Eqn. (26) it was postulated that the mutual approach up to contact leads to irreversible aggregation, and molecular long-range forces were neglected. Hence the stabilisation coefficient introduced by the present author is described by the expression

$$J = \frac{\nu_0}{\nu} = \int_0^\infty e^{\frac{U(H)}{kT}}\frac{2R}{(2R + H)^2}\, dH, \quad (27)$$

where ν_0 is the value of ν for $U(H) = 0$, i.e. in the absence of repulsion forces. Later J was called the retardation coefficient.

Eqn. (25) was supplemented[39,40] by a term defining the energy of attraction of the particles via van der Waals forces and assumed the following form:

$$U(H) = \frac{\varepsilon R\varphi_0^2}{2}\ln(1 + e^{-\varkappa H}) - \frac{AR}{12H}, \quad (28)$$

where A is the Hamaker constant. Analysis of Eqn. (28) showed[39,40] that, for values of the dimensionless parameter

$$m = \frac{1}{6}\frac{A\varkappa}{\varepsilon\varphi_0^2} < 0.3 \quad (29)$$

the function $U(H)$ has a shallow minimum and to the left of it a maximum whose height increases on further decrease of the parameter m (Fig. 3).

On substituting Eqn. (28) in Eqn. (27), it can be shown that the coefficient J is large, provided that

$$\frac{\varepsilon\varphi_0^2}{A\varkappa} > 1. \quad (30)$$

This criterion was introduced for $R \gg d$ and for low electrolyte concentrations where Eqns. (6) and (10) are applicable, subject to the condition that the dimensionless potential of the surface of the particles, corresponding to the coagulation threshold, is fairly small, i.e. that Eqn. (9) holds.

Inequality (30) is a modification and a refinement of the empirical rule of Eilers and Korff[41,42]. It agrees well with Powis's work[43], where observations on stability were accompanied by measurements of the electrokinetic potential ζ.

The substitution of the electrokinetic potential ζ instead of φ_0 in Eqn. (30) is permissible to a first approximation at low electrolyte concentrations. Inequality (30) in a modified form[44,45] proved to be applicable also to the determination of the limits of floatability of natural hydrophobic minerals[46-48].

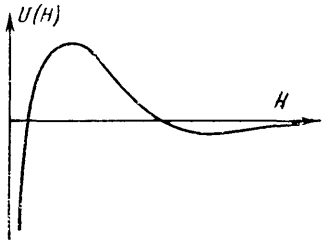


Figure 3. Dependence of the interaction energy between two particles U on the distance H.

An inconvenient aspect of the practical application of inequality (30) is that it includes, apart from the concentration (which determines the values of κ), a second unknown φ_0, which is difficult to measure accurately.

The present author[26-29] also considered another limiting case of the stability of lyophobic colloids corresponding to the condition

$$R \ll d, \tag{31}$$

which obtains either for highly disperse systems or at a very low ionic strength. If the van der Waals interaction is taken into account, then, instead of inequality (30), one must formulate the stability criterion [the condition for the maximum on the $U(H)$ curve] in the following form:

$$\frac{\varepsilon R \varphi_0^2}{A} > 1. \tag{32}$$

In order to ensure that the $U(H)$ maximum is much larger than the energy of the Brownian motion, it is necessary that an additional condition be fulfilled:

$$\frac{\varepsilon R \varphi_0^2}{kT} > 20, \tag{33}$$

which is infringed sooner for low values of A than condition (32).

Either condition [(32) and (33)] should be inevitably infringed for low values of K, i.e. for highly disperse systems, as observed in practice. Barriers preventing both the aggregation and deaggregation of particles are gradually lowered on passing from colloidally disperse systems to true solutions in which they are of the order of magnitude of the energy of Brownian motion or less.

III. THE FREE ENERGY OF CHARGED PARTICLES IN AN ELECTROLYTE SOLUTION

The first studies by the author of this review on the theory of stability were restricted to condition (9), i.e. to the condition where the potential φ_0 is small. The removal of this limitation and replacement of Eqn. (10) by the unsimplified Eqn. (6) was associated merely with computational conditions and was the subject of further studies[49-53]. However, the determination of the correct physical principles for calculations of the interaction between particles when their ionic double layers overlap and rigorous allowance for the van der Waals forces proved to be by no means trivial tasks, as shown by the errors in the 1939 publications by Levine[54-57] and Corkill and Rosenhead[58].

These workers adopted as their next task the calculation of the free energy of colloid particles. Knowing the dependence of the free energy on the distance between the particles, the interaction forces can also be found with some approximation by evaluating the derivative of the free energy with respect to distance. Many followers of these investigators concentrated initially on the calculation of the free energy of the system of charged particles in electrolyte solutions. In order to justify the advantages of this method of calculation on the interaction between colloid particles, Verwey and Overbeek wrote[59] "Serious difficulties arise in the subsequent integration (of the repulsive force) with respect to distance even for planar double layers. Indeed the force in the latter case is not a simple function of distance between the plates and it must therefore be integrated by numerical or graphical methods. In view of these difficulties, we investigated another simpler procedure: the determination of the free energy.... "

One cannot agree with these views, in the first place because the integration of the interaction force can be carried out analytically in terms of very general postulates, in particular when the potential is independent of the distance between the surfaces and when the density of the surface charge of the particles is independent of this distance[60-62]. If it were impossible to integrate analytically the expression for the force, it would also be impossible to obtain this expression in terms of the derivative of the free energy. The fundamental advantages of the "force method" are as follows:

1. The expression for the interaction force can be obtained very simply and rigorously from general and rigorous postulates of electrostatics and hydrostatics, using the familiar expression for the ponderomotive forces in an electric field.
2. The expression is independent of the type of variation of the potential for the surface charge with the distance between the particles and is therefore more general and fundamental.
3. It is easier to introduce corrections into this expression, taking into account the influence of dielectric saturation, the dense ionic layer, the mirror forces and the discrete nature of the ions, and the penetration of electric field into the bulk of the particles.

The history of the calculations of the free energy of the double layers surrounding particles showed that the establishment of the physical principles of these calculations involved considerable difficulties of both fundamental and mathematical kinds, and was fraught with many errors and obscurities. Apart from this, the expression for the free energy, in contrast to the expression for the interaction force, depends on the mechanism of the charging of

the surface particles and is of a different type, for example, in the two limiting cases where either the potential of the particles or the density of the surface charge is independent of the thickness of the intervening layer. It is particularly difficult to calculate the free energy in the case where the surface becomes non-isopotential as the particles approach one another, and the electric field penetrates into the bulk of the colloid particles.

It is therefore superfluous to calculate the free energy of the system in the theory of the interaction of colloid particles and the theory of the stability of colloids based on it, and it is incomparably simpler to employ directly the repulsion forces between particles.

However, the free energy of particles or electrodes immersed in an electrolyte solution is of independent interest. The history of the development of its calculation is extremely instructive and merits a critical consideration.

As stated above, the papers by Levine[54-57] and Corkill and Rosenhead[58] contain an incorrect expression for the free energy of ionic double layers and hence for the energy of the interaction between the particles when their ionic atmosphere overlap. It follows from the formulae derived that identically charged particles should attract one another over long distances, i.e. a qualitatively incorrect result was obtained.

The present paper[63,64] (1940) discovered the root cause of the error and indicated two correct methods for the determination of the free energy of charged particles in an electrolyte solution leading to the same expressions for the interaction forces as those found in his earlier studies[26,27].

The first, purely thermodynamic method is based on the expression for the differential of the free energy of the system of charged spheres immersed in an electrolyte solution. For simplicity, we shall assume that the surface of each sphere is isopotential and that each carries a charge e_i, which does not change in consequence of the ideal polarisability of the surface. Subsequently it will be shown that the combination of the requirements for an isopotential surface and the constancy of the overall charge can only apply approximately†. In a more rigorous treatment it is assumed that a constant potential has been specified on the surface of each particle and that the charge can vary when the ionic atmospheres overlap as the particles approach one another. This treatment corresponds to a different limiting case—the case of ideal non-polarisability of the surfaces of the particles, and obtains approximately if the potential is determined by the adsorbed ions for an extremely high specific energy of adsorption. Thus we can formulate an expression for the free energy of the system:

$$\mathrm{d}\Phi = \sum \varphi_i \mathrm{d}e_i - \sum (X_i \mathrm{d}x_i + Y_i \mathrm{d}y_i + Z_i \mathrm{d}z_i), \tag{34}$$

where φ_i and e_i are respectively the potential and the charge of the ith spherical particle, x_i, y_i, and z_i are its coordinates, and X_i, Y_i, and Z_i are the components of the external forces acting on it. The charges and coordinates of the particles, determining the state of the system when it is in equilibrium, constitute a complete set of its generalised coordinates provided that the surface of each particle is isopotential and non-polarisable.

Terms corresponding to the charges of the ionic atmospheres should not be introduced into Eqn. (34) as was done by Levine, because the coordinates of the ions forming the ionic atmospheres are dependent quantities, in contrast to the coordinates of the particles in the present author's approach, and are established as a result of thermal equilibrium. By integrating Eqn. (34) for fixed positions of the particles, we obtain

$$\Phi = \Phi_0 + \sum \int_0^{e_i} \varphi_i \mathrm{d}e_i, \tag{35}$$

where Φ_0 is the free energy corresponding to the state of the system with uncharged and non-interacting particles and therefore independent of the coordinates. Consequently the part of the free energy associated with the interaction forces is

$$F_e = \sum \int_0^{e_i} \varphi_i \mathrm{d}e_i. \tag{36}$$

The derivatives of F_e with respect to the distances between the particles for e_i = const. give rise to forces of interaction between them and the work performed in the mutual approach of the particles from infinity is given by the following expression according to Eqn. (36):

$$A = F_e - F_\infty = \sum \int_0^{e_i} (\varphi_i - \varphi_\infty) \mathrm{d}e_i. \tag{37}$$

For low potentials, when φ_i and e_i are proportional to one another, we obtain instead of Eqn. (36)

$$F_e = \frac{1}{2} \sum \varphi_i e_i. \tag{38}$$

The free energy F_e can be expressed in terms of the electric fields in the ionic atmospheres. On differentiating Eqn. (36) for constant values of φ_i and ϵ and expressing $\mathrm{d}e_i$ in terms of the value of $\partial\varphi/\partial n$ at the surface‡, we obtain

$$\mathrm{d}F_e = \frac{\varepsilon}{4\pi} \int \varphi \, \mathrm{d}\left(\frac{\partial\varphi}{\partial n}\right) \mathrm{d}S, \tag{39}$$

where n is the coordinate along the normal to the surface of the ith particle, and $\mathrm{d}S$ is an element of the surface; the integration is extended to the surface of all the particles.

Next, on transforming this expression with the aid of Green's theorem and Poisson's equation, we obtain

$$\mathrm{d}F_e = \frac{\varepsilon}{4\pi} \int \left[\frac{\partial\varphi}{\partial x} \mathrm{d}\left(\frac{\partial\varphi}{\partial x}\right) + \frac{\partial\varphi}{\partial y} \mathrm{d}\left(\frac{d\varphi}{\partial y}\right) + \frac{\partial\varphi}{\partial z} \mathrm{d}\left(\frac{\partial\varphi}{\partial z}\right)\right] \mathrm{d}n - \int \varphi \, \mathrm{d}\rho \, \mathrm{d}v; \tag{40}$$

the integration is carried out with respect to the entire volume of the electrolyte (where φ or grad φ are non-zero). Integration of Eqn. (40) yields

$$F_e = \frac{\varepsilon}{8\pi} \int |\mathrm{grad}\,\varphi|^2 \mathrm{d}v - \int_0^{\rho} \int \varphi \, \mathrm{d}\rho \, \mathrm{d}v. \tag{41}$$

The integral $\int_0^{\rho} \varphi \mathrm{d}\rho$ in the second term on the right-hand side of Eqn. (41) can be readily evaluated using the dependence of ρ on φ expressed by the Poisson–Boltzmann equation [Eqn. (6)]. When simplified Eqn. (10), used for low potential, is employed, Eqn. (41) becomes

$$F_e = \frac{\varepsilon}{8\pi} \int |\mathrm{grad}\,\varphi|^2 \mathrm{d}v + \kappa^2 \int \varphi^2 \mathrm{d}v. \tag{42}$$

†Incidentally the results depend also on where the surface separating the surface charge from the diffuse ionic atmosphere is drawn.

‡It is assumed that there are no fields within the particles, for example, by virtue of the isopotential nature of the surfaces.

The second term, introduced by the present author[63], is absent from Levine's equation[54,55], which explains why Levine obtained an incorrect expression for the interaction forces. It was also shown[63] that the free energy of the charged particles satisfies the Gibbs–Helmholtz equation:

$$F_e - T\frac{\partial F_e}{\partial T} = U_e = \left(\varepsilon + T\frac{\partial \varepsilon}{\partial T}\right)\frac{\int |\operatorname{grad}\varphi|^2}{8\pi} d v, \tag{43}$$

where U_e is the total internal energy—the increment in the total electrochemical energy which depends on the electric field. We shall now describe the derivation of Eqn.(43) for the simplest case of conducting particles whose charges have been specified. Denoting the temperature-dependent variation of the quantities by δ and applying Poisson's equation and Green's theorem, we obtain from Eqn. (41)

$$\delta F_e = \frac{\delta\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2 d v - \frac{1}{4\pi}\int \varphi\varepsilon\delta\Delta\varphi\, d v - \tag{44}$$
$$- \int \varphi\delta\rho\, d v - \int d v \int_0^{\rho} \delta\varphi_\rho\, d\rho\, \frac{1}{4\pi}\varphi \int \varepsilon\delta\left(\frac{\partial\varphi}{\partial n}\right) d S$$

where $\partial\varphi/\partial n$ is the derivative with respect to the external normal to the surface of the particle and dS is an element of its surface. In the penultimate term on the right-hand side the integrand $\delta\varphi_\rho$, where φ_ρ is a function of ρ and T, corresponds to a constant value of ρ. We obtain from the Poisson equation

$$\frac{1}{4\pi}\delta(\varepsilon\Delta\varphi) + \delta\rho = 0. \tag{45}$$

The condition of a constant total charge on each particle yields

$$\int \delta\left(\varepsilon\frac{\partial\varphi}{\partial n}\right) d S = 0. \tag{46}$$

With the aid of Eqns. (45) and (46), the expression for δF_e can be put in the following form:

$$\delta F_e = \frac{\delta\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2 d v + \frac{\delta\varepsilon}{4\pi}\int \varphi\Delta\varphi\, d v - \int d v \int \delta\varphi_\rho\, d\rho + \frac{\delta\varepsilon}{4\pi}\int \varphi\frac{\partial\varphi}{\partial n} d S.$$

Application of the Green's theorem yields

$$\delta F_e = -\frac{\delta\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2 d v - \int d v \int \delta\varphi_\rho\, d\rho; \tag{47}$$

whence

$$\frac{d F_e}{d T} = -\frac{d\varepsilon}{d T}\cdot\frac{1}{8\pi}\int |\operatorname{grad}\varphi|^2 d v - \int d v \int \frac{d\varphi_\rho}{d T} d\rho. \tag{48}$$

The Boltzmann equation relates ρ and φ by an expression of the type

$$\rho = \omega\left(\frac{\varphi}{T}\right). \tag{49}$$

where ω is a function of φ/T. Consequently

$$\varphi = T\omega^{-1}(\rho), \tag{49'}$$

whence

$$\varphi - T\frac{d\varphi_\rho}{d T} = 0. \tag{49''}$$

Taking into account Eqn. (49), we obtain Eqn. (43) from Eqns. (41) and (48).

We shall now show that F_e, as given by Eqn. (41), is also obtained by an artificial procedure based on the consideration of an imaginary ion charging process and applied by Debye to the calculation of the electrical component of the free energy of strong electrolytes. The correct§ application of the Debye method for particles surrounded by ionic atmospheres has been described[63,64]. An analogous derivation (with certain differences) was described by Casimir[65]. The Debye method involves the consideration of the work of an imaginary process in which all the ions are charged simultaneously and at each instant the charges of the ions and of the particles are equal to the real charges multiplied by a parameter λ, which varies in the charging process from 0 to 1, but is independent of the coordinates of the given ion. As a result, the charge densities of the ionic atmosphere should vary in proportion to this parameter.

It is easy to show that, in calculations on the work of the charging process, which depends on the charges of the particles, it is sufficient to take into account only the macroscopic field around the charges (i.e. the average force potential), neglecting the microfields of the atmospheres around the individual ions, which are considered in the Debye theory of strong electrolytes. The elemental work dA of the charging process, corresponding to the increment $d\lambda$ in the parameter λ, is then given by

$$d A = \sum \varphi_i e_i d\lambda + \int \varphi_\lambda \rho_\lambda \frac{d\lambda}{\lambda} d v, \tag{50}$$

where e_i are the charges of the particles; the subscript λ shows that the corresponding quantities refer to the instant of charging, corresponding to the given value of the parameter λ. If the surfaces of the particles are not isopotential, e_i denotes the charges of elementary sections of their surfaces, and the summation sign Σ should be replaced by the integration sign with respect to the surfaces of all the particles. The charges of the particles play a role analogous to the charges of the ions, i.e. the surfaces of the particles behave during the charging process as ideally polarisable electrodes and their charges cannot vary as a result of adsorption.

One can therefore write

$$e_i d\lambda = e_{i\lambda}\frac{d\lambda}{\lambda} = d e_{i\lambda}. \tag{51}$$

On the other hand, one cannot put

$$\rho_\lambda \cdot \frac{d\lambda}{\lambda} = d\rho_\lambda \tag{52}$$

as in Levine's work[54-56], since the increment in the charge density in the ionic atmosphere with increasing λ takes place not only in consequence of the increase by $d\lambda/\lambda$ of the charges of the ions forming part of the ionic atmosphere at a given instant, but also in consequence of a redistribution of the ions between the atmosphere and the bulk of the solution. This redistribution takes place with increase of λ owing to the change in the constants a and α which depend on the ionic charge and relate in accordance with the Boltzmann equation the concentration of the ions in the double layer and the potential φ.

We shall now prove the relation

$$d A = d F_{e\lambda}, \tag{53}$$

where $F_{e\lambda}$ is the value of F_e in a hypothetical fictitious case, where the charges are reduced by a factor λ. In calculating $dF_{e\lambda}$ one must bear in mind that the relation

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§An incorrect use of the Debye method in this case[54-56] led to a value of F_e different from that of the present author and agreeing with the value obtained when only the first term is retained on the right-hand side of Eqn.(41).

$\varphi(\rho)$ is also modified by virtue of the change in the constants a and α, which depend on λ.

We obtain from Eqn. (40) [the derivation is the same as that of Eqn. (44) but it is now assumed that $d\epsilon = 0$]:

$$dF_{e\lambda} = -\frac{\varepsilon}{4\pi}\int \varphi_\lambda d\Delta\varphi_\lambda dv - \int \varphi_\lambda d\rho_\lambda dv - \\ -\int dv \int_0^{\rho_\lambda} d\varphi_\lambda d\rho_\lambda - \frac{\varepsilon}{4\pi}\int \varphi_\lambda d\left(\frac{\partial\varphi_\lambda}{\partial n}\right) dS, \quad (54)$$

or, taking into account the Poisson and Gauss equations

$$dF_{e\lambda} = -\int dv \int_0^{\rho_\lambda} d\varphi_\lambda d\rho_\lambda + \sum_i \varphi_{i\lambda} de_{i\lambda}. \quad (55)$$

Taking into account the identity

$$\left(\frac{\partial\varphi_\lambda}{\partial\lambda}\right)_{\rho_\lambda} = -\left(\frac{\partial\varphi_\lambda}{\partial\rho}\right)_\lambda \cdot \left(\frac{\partial\rho_\lambda}{\partial\lambda}\right)_{\varphi_\lambda}, \quad (56)$$

we obtain instead of Eqn. (55)

$$dF_{e\lambda} = \sum_i \varphi_{i\lambda} de_{i\lambda} + \int dv \int_0^{\varphi_\lambda} d\lambda \left(\frac{d\rho_\lambda}{d\lambda}\right)_{\varphi_\lambda} d\varphi_\lambda. \quad (57)$$

According to Eqn. (6), ρ depends on the ionic charge z and hence also on λ via the coefficients a and α in the equation

$$\rho = af(\alpha\varphi). \quad (58)$$

which are proportional to the ionic charge. One can therefore easily demonstrate the identity

$$z\left(\frac{\partial\rho_\lambda}{\partial z}\right)_\varphi = \lambda\left(\frac{\partial\rho_\lambda}{\partial\lambda}\right)_\varphi = \frac{\partial\rho_\lambda\varphi_\lambda}{\partial\varphi_\lambda}. \quad (59)$$

On substituting Eqn. (59) in Eqn. (57) and integrating the latter, we obtain finally,

$$dF_{e\lambda} = \sum \varphi_{i\lambda} de_{i\lambda} + \int \rho_\lambda\varphi_\lambda \frac{d\lambda}{\lambda} dv. \quad (60)$$

The validity of Eqn. (53) follows from a comparison of Eqn. (60) with Eqns. (50) and (51). On integrating the latter in the range from 0 to 1, we obtain

$$A = F_e. \quad (61)$$

Thus the correct generalisation of the Debye method leads to the same correct Eqn. (36) for the free energy of the particles in the electrolyte solution.

The function F_e, specified by Eqn. (36) is, by virtue of Eqn. (7), the potential of the interaction of the particles in the electrolyte solution at a constant charge on each particle. However, Eqn. (41) can be used to find F_e, integrating with respect to the volume of the dispersion medium only, subject to the condition that there is no field within the particles when their surfaces are isopotential. However, on the sections of the surfaces whose ionic atmospheres overlap with the atmospheres of neighbouring particles, the isopotential condition is incompatible with the condition of a constant surface charge density[66,67]. Because of this, the constancy of the overall charge of the particle can be maintained when it approaches another particle only as a result of a change in the charge density on the sections of the surface remote from the overlap zone. However, on these sections, the local surface charge density, which is a function of the local potential, cannot vary as a function of the situation on the sections of the surface remote from it. Thus we conclude that in the case of real colloid systems with an electrolyte solution as the dispersion medium, in which we are interested, where the function F_e should be used in the calculation on the interaction arising following the overlap of the ionic atmospheres, it is impossible to reconcile the conditions of a constant charge and a constant potential. This constitutes the profound difference between this case and classical electrostatics where conducting particles immersed in a liquid dielectric are considered.

In the absence of isopotential conditions, part of the work expended on the charging of the surface of the particles, which is equal to F_e, is consumed in creating an electrostatic field within the particles. In this case appropriate corrections must be applied to Eqns. (39) and (42). Eqns. (43) and (61) remain unchanged, but their derivation must be modified by taking into account the presence of the field within the particles. The cases with a constant potential and a constant charge have been compared[68].

We shall now consider the interaction potential F_φ of the particles at a constant potential (but not charge) of each, which applies particularly to metallic particles with a polarisable surface. The work performed to alter the configuration of the system for constant potentials φ_i is coupled with the work necessary to alter the charges and performed against forces maintaining a constant potential. Consequently we must write instead of Eqn. (37)

$$A_\varphi = \sum \varphi_i^0 (e_i^\infty - e_i^0) = \sum \int_0^{e_i^0} (\varphi_i)\, d e_i - \sum \int_0^{e_i^\infty} \varphi_i d e_i, \quad (62)$$

where the superscripts ∞ and 0 denote the states of the system where the particles are separated by distances for which the ionic atmospheres do not and do overlap respectively, and φ_i^0 is the constant potential applied to the ith particle. On transforming Eqn. (62), we obtain instead of Eqn. (37)

$$A_\varphi = -\sum \int_0^{\varphi_i^0} (e_i^0 - e_i^\infty)\, d\varphi_i = F_\varphi^0 - F_\varphi^\infty. \quad (63)$$

whence it follows that the free energy of the system for a constant potential of the particles is

$$F_\varphi = -\sum \int_0^{\varphi_i} e_i\, d\varphi_i. \quad (63')$$

On differentiating this expression and carrying out transformations analogous to those used in the derivation of Eqn. (39), we obtain

$$dF_\varphi = -\frac{\varepsilon}{4\pi}\int \frac{\partial\varphi}{\partial n} d\varphi\, dS. \quad (64)$$

Application of Green's theorem yields

$$dF_\varphi = -\frac{\varepsilon}{4\pi}\int \left(\frac{\partial\varphi}{\partial x} d\frac{\partial\varphi}{\partial x} + \frac{\partial\varphi}{\partial y} d\frac{\partial\varphi}{\partial y} + \frac{\partial\varphi}{\partial z} d\frac{\partial\varphi}{\partial z}\right) dv - \frac{\varepsilon}{4\pi}\int \Delta\varphi\, d\varphi\, dS, \quad (65)$$

or, taking into account Poisson's equation and integrating, we obtain

$$F_\varphi = -\frac{\varepsilon}{8\pi}\int |\operatorname{grad}\varphi|^2 dv + \int dv \int_0^{\varphi} \rho\, d\varphi. \quad (66)$$

Here ρ is a function of φ, specified by the Boltzmann equation (3) or Eqn. (58).

Eqns. (64) and (66) differ from Eqns. (39) and (41), which express the free energy of the electric field in the electrolyte, because they take into account, apart from the energy of the field, the energy of the source of the charge used to maintain a constant potential of the surfaces of the particles.

We shall now prove that Eqn.(41) or (66) is equivalent to the system of tensions of the Maxwell electric field tensor to which an excess isotropic hydrostatic pressure has been added:

$$p = \int_0^{\varphi} \rho \, d\varphi. \tag{67}$$

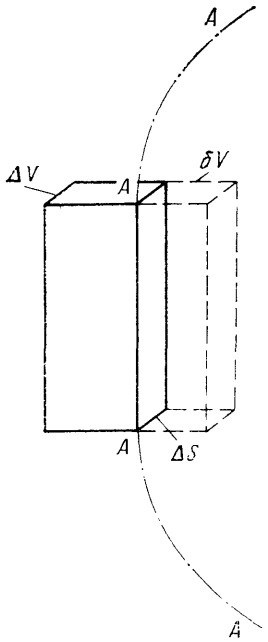


Figure 4. Derivation of the pressure tensor in an electrolyte surrounding charged particles.

We isolate from the total volume of the electrolyte a volume element Δv (Fig.4) and consider the virtual work performed in its expansion as a result of the displacement of a small section of its surface ΔS by a distance δh into the bulk of the remaining volume. The work expended in this process is converted into an increment of the free energy δF_{φ} of the remaining part of the system, in relation to which the volume V plays the role of the external medium:

$$\delta A = P\delta V = \delta F_{\varphi}, \tag{68}$$

where P is the total (including the corresponding component of the Maxwellian tensor) pressure on the given section of the surface of the volume and $\delta V = \Delta S \delta h$ is the volume increment ΔV when a section ΔS of its surface is displaced. The variation of δF_{φ} is given by the sum of two terms:

$$\delta F_{\varphi} = \delta_1 F_{\varphi} + \delta_2 F_{\varphi}. \tag{69}$$

The first term expresses the change in F_{φ} as a result of the loss of the field element δV and is therefore equal to

$$\delta_1 F_{\varphi} = +\frac{\varepsilon}{8\pi} |\operatorname{grad}\varphi|^2 \delta V - \int_0^{\varphi} \rho \, d\varphi \delta V. \tag{70}$$

The second term in Eqn.(69) expresses the change in F_{φ} occurring owing to the change in the potential φ over the entire volume of the system due to the shift of a section ΔS of the outer surface. The change $\delta_2 F_{\varphi}$ would be zero if, following the shift of the surface, its potential, having changed, acquires the value which existed hitherto at its new location, having received thereby the increment

$$\delta\varphi = \frac{\partial\varphi}{\partial n} \delta h, \tag{71}$$

where $\partial\varphi/\partial n$ is the derivative of φ with respect to the normal to the surface at the point under consideration.

However, the applicability of Eqn.(68) is determined by the maintenance on all the boundaries of the solution of the electrolyte AAAA (Fig.4) of a constant potential (this is recalled by the subscript φ in F_{φ}); in reality there is therefore no increment in the potential φ defined by Eqn. (71) and the new values of the potential at the new site on the surface S are reduced compared with the previous ones by an amount

$$\delta\varphi = -\frac{\partial\varphi}{\partial n} \delta h. \tag{72}$$

We can find from Eqn.(66) the change in F_{φ} caused by this factor:

$$\delta_2 F_{\varphi} = -\frac{\varepsilon}{4\pi} \int (\operatorname{grad}\varphi \cdot \operatorname{grad}\delta\varphi) \, dv + \int \rho\delta\varphi \, dv. \tag{73}$$

Application of Green's theorem yields

$$\delta_2 F_{\varphi} = \int \left(\frac{\varepsilon}{4\pi}\Delta\varphi + \rho\right)\delta\varphi \, dv + \frac{\varepsilon}{4\pi}\int \frac{\partial\varphi}{\partial n}\delta\varphi \, dS. \tag{74}$$

Taking into account Poisson's equation and Eqn.(72), we obtain

$$\delta_2 F_{\varphi} = -\frac{\varepsilon}{4\pi}\int \left(\frac{\partial\varphi}{\partial n}\right)^2 \delta h \, dS = \frac{-\varepsilon}{4\pi}\left(\frac{\partial\varphi}{\partial n}\right)^2 \delta V. \tag{75}$$

Finally, we find from Eqns.(75), (70), (69), and (68)

$$P = \frac{\varepsilon}{8\pi}|\operatorname{grad}\varphi|^2 - \frac{\varepsilon}{4\pi}\left(\frac{\partial\varphi}{\partial n}\right)^2 - \int_0^{\varphi} \rho \, d\varphi. \tag{76}$$

The last term on the right-hand side of Eqn.(76) expresses the excess isotropic hydrostatic pressure which is due to the electric field within the framework of the applicability of the Boltzmann equation and which depends on the field potential φ in accordance with the equation

$$p = -\int_0^{\varphi} \rho \, d\varphi = kT \sum c_i (e^{-\alpha_i\varphi} - 1), \tag{77}$$

which is applicable to any electrolyte including an asymmetric electrolyte.

The sum of the first two terms in Eqn.(76) expresses the pressure of the electrostatic field, which follows from the Maxwell tensor.

In the specific case of a plane parallel to the lines of force of the field, we have

$$P_{\parallel} = \frac{\varepsilon}{8\pi}|\operatorname{grad}\varphi|^2 + p. \tag{78}$$

The formula corresponding to a plane at right angles to the field vector is

$$P_{\perp} = -\frac{\varepsilon}{8\pi}|\operatorname{grag}\varphi|^2 + p. \tag{79}$$

It is important to emphasise that the values of the pressure P obtained are independent of the conditions governing the maintenance of the potential or charge when the surfaces

are displaced. Eqns.(78) and (79) can be undoubtedly obtained also by considering the function F_e.

Eqn.(79) agrees with Eqn.(1) which we used previously and confirms it.

According to its derivation, Eqn.(76) is applicable to any plane selected within the bulk of the electrolyte. This makes it possible to calculate the interaction forces between two particles by the summation of the pressure, expressed by Eqn.(76), over all the sections of any surface incorporating one of the particles or with respect to any infinite plan BB′ separating them (Fig.5). Indeed, according to Stevin's solidification principle, equilibrium cannot be infringed if part of the liquid, included between this surface and the particle which it incorporates, "solidifies" (without change in charge density and distribution). The condition for equilibrium in the solidified part requires that the forces balancing the pressures on the outer and inner surfaces bounding this region should be equal since the introduction of the Maxwell tensor excludes from consideration the long-range electrical forces applied to the charges of the ionic atmospheres. However, the force balancing the pressure on the inner surface is equal to the force acting on the particle itself. Mathematically it is most convenient to select the symmetry plane normal to the line passing through the centres of two identical spherical particles (BB′ in Fig.5) as the separating surface for two such particles. In this case one must integrate with respect to this plane the pressure expressed by Eqn.(78), which was done by the present author [63,64] and by Dukhin et al. [69].

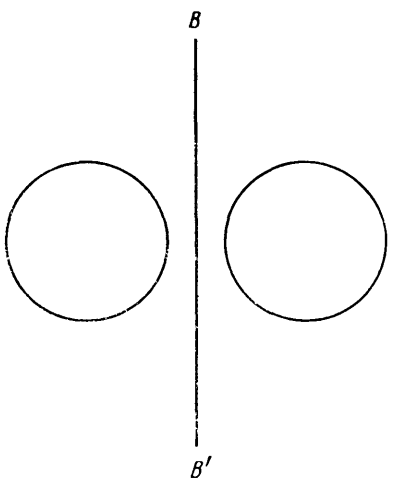


Figure 5. Calculation of the degree of interaction between spherical particles.

It follows from Eqn.(78) that the interaction of a sphere with a plane, which remains uncharged under all conditions, is the same as its interaction with another identical sphere. In addition one must take into account the fact that the boundary conditions in these problems are such that the distribution of the potential is the same in both instances. For two spheres charged to potentials which are equal but of opposite sign, it is possible to apply Eqn.(79) having put $p = 0$. Since the potential is zero at all points on the symmetry plane and p depends on φ in accordance with Eqn.(4) or (77), Eqn.(79) with $p = 0$ is also applicable to the calculation of the attraction is an electrolyte solution of a charged particle to the surface of a conductor with a zero potential. This case obtains, for example, in the electrophoretic coatings. We may note that Ikeda [70] arrived at the same expressions for the free energy and hence for the interaction forces of the particles in electrolyte solutions on the basis of a rigorously statistical method.

In conclusion of this section, we shall indicate a method for the calculation of the interaction forces between parallel plates in an electrolyte solution [72], which is based on a generalisation of the Gibbs–Duhem equation [71] in combination with the Poisson–Boltzmann equation. This method employs the most general postulates of thermodynamics and statistics, does not require the introduction of any additional assumptions, and does not use the Maxwell tension tensor and the distribution of the hydrostatic pressure in ionic double layers. For this reason, this is the most rigorous and general method, being at the same time very simple mathematically.

Further application of the above principles to the theory of the stability of lyophobic colloids has been described by the present author and Landau [52,53]. In contrast to previous reports, they calculated the repulsion forces from exact formulae obtained without linearising the Poisson–Boltzmann equation. At the same time, as in earlier studies [39,40], account was taken of the dispersion type attraction forces. For the interaction between plates separated by a plane-parallel layer of electrolyte, this implies that the wedging pressure of the layer [73–78] is considered as the sum of two terms—electrostatic and molecular (negative), which is characteristic of lyophobic systems. The degree of interaction between spherical particles was calculated on the basis of the interaction between plane surfaces by the integration method proposed previously [37].

It was shown that in the general case the curves describing the potential interaction energy can have, as before [26,29,39,40] (Fig.3), a potential barrier, which prevents particles from entering the potential well.

The present author and Landau [52,53] examined the limiting case of highly charged species and found conditions under which the potential and force barriers separating them vanish. The calculations were performed both for a symmetrical electrolyte and for electrolytes of the 1-2 and 2-1 valence types (the first numeral indicates the charge of the counterion). It was demonstrated by these examples that the charge of the coion has little effect on the stability of the sol. On the other hand, the charge of the counterion ez_1 determines the coagulation concentration m in accordance with the formula

$$m = C\frac{\varepsilon^3 (kT)^5}{A^2 e^6 z_1^6}, \qquad (80)$$

where A is the Hamaker constant and C a numerical coefficient, which depends only slightly on the valence of the coion. Thus the Hardy-Schulze rule, which states that the valence of the counterion has a dominant and a strong influence on the coagulation threshold, was explained.

The coagulation criterion (80), derived theoretically by the present author and Landau, is in good agreement with many experimental data which have accumulated in the last thirty years [79,80]. For convenience, it is frequently formulated in the form:

$$m \propto z_1^{-6}. \qquad (81)$$

In many instances deviations are observed, which can be accounted for by the lack of validity of the postulates underlying the derivation of this criterion: for example, the solvation of the surfaces of the particles and the failure of the condition that the Debye length is small compared with the radius of the particles. It is more difficult to explain why condition (80) is valid even when the dimensionless potential of the particle

$$\omega = \frac{z_i e\psi}{kT} \tag{82}$$

is small, so that one of the main conditions underlying its derivation does not hold. This question was considered particularly by Muller[81]. Glazman and Dykman[82,83] formulated the condition governing the applicability of the "law" defined by Eqn.(81) for moderate values of ω; this condition, which is of the form

$$\omega \propto z_i\varphi = \text{const}, \tag{83}$$

involves an inverse proportionality between the potential of the particle and the charge of the counterion. Us'yarov[84] demonstrated in relation to extensive experimental data that this condition holds satisfactorily in practice, and interpreted it theoretically.

It is noteworthy that the correct formulae for the repulsion forces between particles with a specified charge, separated by plane-parallel layers of electrolytes at any potential, have been developed by Bergmann et al.[49] in an attempt to explain the formation of the so-called "schiller" layers¶. These layers are formed after the sedimentation of lamellar particles of certain minerals in an electrolyte solution. The thicknesses of the layers separating the particles at different electrolyte concentrations can be determined from the interference colours visible in the light reflected from them. These thicknesses proved to agree more or less with theoretical calculations in which the pressure on the layer was calculated from the weight of the particles located above them. The effect of van der Waals forces was not taken into account, which apparently did not introduce a significant error. Bergmann et al.[49] confirmed experimentally the theory of the repulsion forces in electrolyte layers, but did not claim to have established a general theory of the stability of lyophobic colloids. The theory of the stability of lyophobic colloids was developed further by Verwey and Overbeek[31]. Their investigations were based on the principles described above. Apart from publication of a monograph on the subject, they can be credited with the study of the following problems:

1. The use of formulae for the repulsion forces between colloid particles charged to any potential.
2. The elucidation of the influence of the Stern correction, which takes into account the formation of a dense monolayer of adsorbed ions on the stability of colloids.
3. A theoretical determination of the principal characteristics of peptisation process.
4. Examination of the influence of the secondary (remote) potential well, first observed by the present author[39], on the aggregation and thixotropy of suspensions.

¶The name of these layers originates from the German word *schillern*, meaning to iridesce, which has apparently been long forgotten. On the erroneous assumption that this name is derived from the name of a scientist, they have come to be called Schiller layers.

IV. ALLOWANCE FOR MONOLAYER ADSORPTION

A correction taking into account the monolayer adsorption on the basis of the Stern or some other theory is of the most fundamental importance for the refinement of the theory of the stability of lyophobic colloids. On the basis of the Stern theory in a simplified form, Verwey and Overbeek arrived at the following conclusions.

In the Stern layer AA'SS' (Fig.6) there is a sharp decrease of potential (continuous UU' curve), which forces the potential of the diffuse layer to assume a Stern potential U' significantly smaller than the potential of the surface of the particle itself. This decrease of the potential eliminates objections to the employment in the theory of stability of the Boltzmann equation for potentials at which an unrealistically high concentration of ions is obtained. Furthermore, the introduction of the Stern correction improves the agreement between the theory and experiment, since it makes it possible to explain the dependence of the coagulating action of the counterions having the same charge on their chemical nature (their position in the lyotropic series). The Stern correction makes it possible to eliminate also a number of other contradictions, but some inconsistencies between theory and experiment nevertheless remained. Thus the Deryagin–Landau–Verwey–Overbeek (DLVO) theory explains the linear dependence of the logarithm on the concentration of the added indifferent electrolyte[86]. However, the experimental dependence of the slope of the plot of this function against the radius of the particles and the valence of the counterion does not agree with this theory[87].

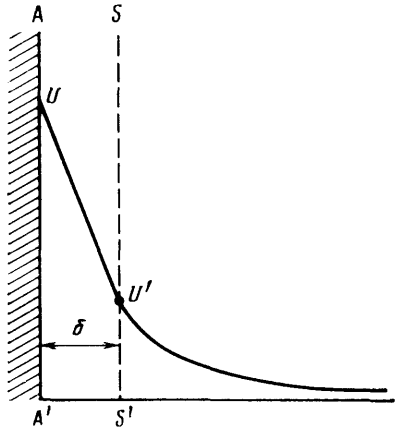


Figure 6. Distribution of the potential in the double layer near a charged surface.

An attempt to improve the DLVO theory by taking into account additional factors has been made by Martynov and Muller[88,89]. Their calculations include the earlier hypothesis that the presence of a molecular condenser shifts the plane corresponding to the beginning of the diffuse layer by a distance equal to its thickness δ relative to the interface (in their calculations the authors assumed that $\delta = 4$ Å). Thus the distance, inversely related to the van der Waals interaction, increases by 2 δ. The author's calculate that this can cause the near-by potential well to vanish

before the potential barrier under the influence of uni-univalent electrolytes. At a Stern potential exceeding 25–50 mV and at fairly high electrolyte concentrations, the near-by potential well disappears for similar values of the parameters for both planar surfaces and for spherical particles.

This conclusion conflicts with a multiplicity of experimental studies[6], which have firmly established the existence of two potential wells for electrolytes of different valence, including uni-univalent electrolytes, and for low concentrations and high potentials. The presence of a near-by potential well, protected by a potential barrier, has been observed particularly clearly in a study of the intracrystalline swelling of montmorillonite saturated beforehand by ion exchange with lithium, sodium, or potassium cations.[90] The problem has been studied theoretically by Serebrovskaya et al.[91] Comparison of the calculations with experiment showed that the quantitative discrepancies may be accounted for by the shear strength of the interlayer aqueous layers. Another possible cause, which reduces the thicknesses of the aqueous layers observed at low ionic strengths is, according to Van Olphen[92], adhesion of small crystals to the edges of other small crystals. Both explanations require further tests. There have also been a number of studies[93] indicating unambiguously the existence in various colloid systems of two wells separated by a barrier. For periodic colloid structures, the transfer of particles from the remote potential well to the near-by well is examined by direct microscopic observations[94,127].

The inconsistency between the conclusions in the literature[88,89] and experimental data is not surprising when the principles from which they were derived are examined more deeply. In the first place the concept of a molecular condenser whose charges are uniformly "smeared" over parallel planes is applicable in the introduction of a correction to the distribution of the potential (and hence to the repulsion forces) only at distances from the interfaces significantly exceeding the distance between neighbouring ions in the adsorption monolayer. Furthermore, the distance of the near-by potential well is known not to satisfy this necessary condition, particularly at electrolyte concentrations for which a barrier-free coagulation mechanism is said[88,89] to operate, because at these concentrations ($c \simeq 0.1$–0.15 M) the effective Debye thickness of the double layers becomes less than 10 Å. Furthermore, the limit of the applicability of the Poisson–Boltzmann equation, used for the double layer, is reached, since the distance between the surfaces and the near-by potential well becomes of the same order of magnitude as the distance between neighbouring ions of the molecular condenser, but with the thickness of the latter doubled. For this reason the use in this case of the concept of a molecular condenser with an arbitrary thickness in order to infer whether or not a near-by potential well is present is not justified.

This does not imply that the problem of the presence of the potential well cannot be the subject of theoretical calculations, but they must be performed differently taking into account in the first place the discrete nature of the structure of the monolayer of the adsorbed ions.

The last comment is of extremely general importance. The discrete nature of the adsorbed layer, made up of individual ions, must be taken into account also in other instances, for example, when the height of the potential barrier is considered at high electrolyte concentrations. The influence of the discrete structure of the surface charge on the interaction of the planes separated by a layer of electrolyte was taken into account for the first time by Yalamov[95], who used Levine's charging method as corrected by the present author. Using the same method, similar results were obtained recently by Richmond[96]. It was assumed in the above studies that ions are distributed on the surfaces in a strictly periodic arrangement among the sites of identical lattices, i.e. there is a rigorous correlation between the positions of the ions on both planes.

In contrast to these calculations, Deryagin and Muller[97] carried out an approximate stochastic calculation of the influence of the discrete nature of the structure of the dense part of the double layer on the interaction of parallel surfaces at short distances on the assumption that the correlation between the relative positions of the ions adsorbed on opposite surfaces are determined exclusively by the energy of the interaction of these ions in accordance with the Boltzmann equation. In other words, either the ions are adsorbed in a non-localised manner or the positions of the centres of adsorption on a single surface are in no way correlated with the positions of the centres of adsorption on the other surface.

Calculations performed on the assumption that the adsorption energy is small showed that the discrete but disordered distribution of adsorbed ions can reduce sharply the repulsion forces between surfaces over short distances and can thereby deepen the near-by potential well.

It is also important to take into account the discrete structure of the adsorption layer in the calculation of its influence on the Stern potential, i.e. on the potential in the plane from which the diffuse part of the double layer begins. Evidently this transition from the discrete lattice of the adsorption layer to the diffuse layer (treated in macroscopic terms), whose properties depend solely on one coordinate—the distance to the interface—cannot occur abruptly, especially directly on the surface of the outer plate of the condenser. Thus there should be a transitional layer between the molecular condenser and the diffuse ionic atmosphere with a thickness greater than that of the condenser itself. Its existence should alter the calculations of the potential outside its limits and in the diffuse double layer, especially within the transition layer. The thinner the layer of electrolyte, the greater the error in calculations where the effect of the discrete nature of the structure is ignored.

Without taking into account the discrete nature of the Stern layer, it is also impossible to devise a genuine quantitative theory of peptisation processes which, however, did not prevent a qualitative treatment of this phenomenon by Verwey and Overbeek[31] in accordance with experiments and a correct elucidation of its mechanism. Overbeek wrote later[98], "Quantitative studies in this field are lacking, which is to be regretted, since the peptisation phenomenon might yield information about the region of potential curves least accessible to study, corresponding to short distances between particles."

V. THE REVERSIBLE NATURE OF LONG-RANGE AGGREGATION

In their consideration of the problem of the role of the secondary (remote) potential well, Verwey and Overbeek[31] drew attention to the fact that it can be the cause of the formation of aggregates from primary particles only when the radius of the particle is approximately 1 μm and above, i.e. in suspensions. Only then is the depth of the remote

potential well sufficiently large compared with the energy of Brownian motion. Aggregation in the remote well is readily reversible owing to the absence of a barrier hindering the decomposition of aggregates. The aggregation process in the remote well is therefore rapidly balanced by the opposed deaggregation process and the authors used the Boltzmann equation in the following form in order to determine the degree of aggregation:

$$\Delta b = n_0 \int 4\pi a^3 s^2 e^{-V/kT} \, ds, \qquad (84)$$

where Δb is the fraction of aggregated particles, n_0 their total number, $s = d/2R$ (d is the distance between the centres of the particles and R their radius), and V is their interaction energy.

The authors [85] used $\Delta b \geqslant 0.1$ as the aggregation condition. On the basis of Eqn.(84), Martynov and Muller[88,89] found that rapid coagulation takes place when $\Delta b \gg 10$. However, they attribute a completely different significance to the concept of "rapid coagulation" in contrast to that associated with the kinetics of barrier coagulation. The degree of aggregation has been characterised[88,89] by the value of Δb, which depends significantly not only on the depth of the secondary potential well but also on the numerical concentration of the particles. We shall return to the problem of the role of the remote potential well in subsequent discussion of the question of quasi-equilibrium and equilibrium systems in which the particles are interrelated owing to these wells.

In principle, Eqn.(84) is applicable to the calculation of the degree of aggregation also due to the near-by potential well. The difference between the short-range aggregation and long-range aggregation consists in the fact that the corresponding equilibrium is established over a period the duration of which can be very large if the potential barrier is many times greater than the energy kT. Another, less fundamental difference is that the calculation of the interaction energy of the particles in the vicinity of the near-by potential well, for not unduly high electrolyte concentrations when the electrostatic interaction can influence its position and depth, is extremely difficult—one can actually say that so far it is virtually impossible. However, without such calculation, Eqn.(84) cannot be used for quantitative conclusions.

The calculation of the potential barrier and of the conditions for its disappearance is much easier. The results of our calculations, which have been introduced into Fuch's formula[26,38], made it possible to calculate the rate of slow coagulation. In order to test the theory, it is sufficient to measure the number of particles (including primary particles and aggregates) as a function of time. However, until recently these measurements were hindered by the lack of a sufficiently accurate, rapid, and convenient method for counting particles. The method based on the ultramicroscope counting of particles in a stationary volume is relatively unsuitable for this purpose. A number of new methods[99,100] are inconvenient because, owing to the low upper limit to the measurable concentrations, the measurement must be preceded by a high dilution of colloid systems with an optically clear solvent.

New possibilities arose after the development by the present author and Vlasenko of flow ultramicroscopy, initially for counting particles in aerosols[101-103]. Flow ultramicroscopes based on the same principle, for colloid systems with a liquid dispersion medium, have been developed by the present author and Kudryavtseva[104,105]. A series of studies on the kinetics of slow and rapid coagulation of red and blue gold sols have been carried out with the aid of a flow ultramicroscopic method[106,107] at different electrolyte concentrations; a version of the method using a laser has been published[108].

The results obtained permit the following conclusions.

At fairly high electrolyte concentrations the rate of coagulation expressed in terms of the variables $1/n$ and t, where n is the numerical concentration of the particles and t the time elapsed from the onset of coagulation, is expressed, in conformity with Smoluchowski's theory, by a straight line with a slope fairly close to the theoretical value. The deviations from theory can be explained in some cases by the operation of van der Waals forces and in others by deviations from Stokes' law when the particles which have approached one another to distances less than their radii move towards one another[109-111].

With decrease of the electrolyte concentration, the rate of coagulation not only falls but, "in conflict with both the Smoluchowski and Fuchs theories", the dependence of $1/n$ on t deviates increasingly from linearity, the curve becoming S-shaped. Fig. 7 illustrates examples of such relations. At a fairly low electrolyte concentration the reciprocal of the concentration of particles $1/n$, having increased with time by a factor of 2 or more, reaches fairly rapidly a value which remains constant for a long time. This time can increase to many days as the electrolyte concentration is reduced. After the elapse of a certain time, the quantity $1/n$ again begins to increase with t (at any rate for not unduly low electrolyte concentrations) and the curve rises more steeply. Towards the end, the slope of the curve tends to a more or less constant value.

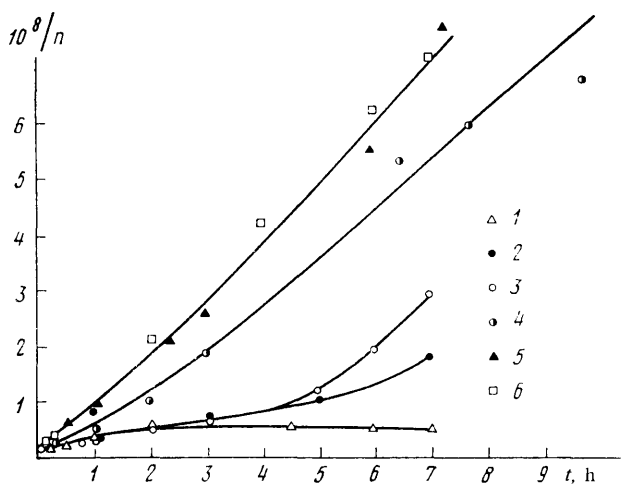


Figure 7. Relation between the reciprocal of the numerical concentration n and the time t. Silver iodide sol; $BaCl_2$ electrolyte; molar electrolyte concentration: *1*) $1.5 \cdot 10^{-3}$; *2*) $1.8 \cdot 10^{-3}$; *3*) $1.9 \cdot 10^{-3}$; *4*) $2.0 \cdot 10^{-3}$; *5*) $2.15 \cdot 10^{-3}$; *6*) $3.0 \cdot 10^{-3}$.

In order to explain this shape of kinetic coagulation curves, the present author and Kudryavtseva took into account the superposition of a deaggregation process on the aggregation process leading to the pairing of particles[106,107]. As a result, the kinetics of this stage of the

coagulation process become similar to those of a reversible bimolecular reaction and obey the differential equation

$$\frac{dn}{dt} = -kn^2 + l(n_0 - n), \quad (85)$$

where n_0 and n are respectively the number of particles at the initial instant and after time t and k and l are constants. The reasons why the equilibrium between the two process breaks down may be twofold:

1. At a certain instant an aggregate may be formed where the energy of the bonds between particles is greater than the energy of the bonds in the remaining aggregates as a result of a kind of collective interaction. For example, if each particle in an aggregate of three particles is linked to two others, then, as a result of the decreased probability of decomposition, the number of particles in the aggregate may subsequently increase rapidly. The growth of the aggregate may acquire the properties of an avalanche is each new particle added to the aggregate forms more than a single bond with any one particle in its condensation. The new state of aggregation equilibrium, at extremely low concentrations of individual particles, may be attained after a very long time.

2. Initially the pairing of particles may occur in the remote potential well. After some time they may pass to the near-by potential well, which sharply increases the bond energy. This facilitates the formation and growth of larger aggregates. It is noteworthy that the depth of the remote potential well for highly disperse sols is so small that the probability of such two-stage process is low.

The formation after a more or less prolonged "latent" period of larger aggregates, which serve, as it were, as effective coagulation nuclei, is clearly confirmed by visual observations in a flow ultramicroscope.

We may add that the cardinal difference between coagulation processes and typical processes involving the formation of new condensed phases consists in the possibility of bonds between particles in an aggregate corresponding to either the primary or secondary (remote) potential minimum. In the former case the barrier mechanism has no adequate analogue in condensation processes. Thus the activation energy for chemical condensation is not determined by the need to overcome repulsion forces as a result of thermal motion, but is caused by the low probability of collisions leading to the activated complex. This difference must be specially emphasised, since any attempt to minimise the fundamental differences between colloid and true solutions interferes with the development of colloid science as an independent discipline and with the discovery of its characteristics.

As stated at the beginning of this review, another characteristic difference between colloid systems and molecular solutions is the existence of two different types of equilibrium—the aggregation equilibrium and the equilibrium of the disperse phase composition. Kudryavtseva et al.[113] reported observations of equilibrium between the coagulant and single gold particles at a numerical concentration of the latter of the order of 10^6 cm^{-3}. However, this does not allow any general conclusions about the reversibility of hydrophobic sols, because, in view of the characteristics of the method developed by Sigmund for the preparation of the red gold sols, a certain degree of hydrophilisation of the surface of its particles due to the adsorption of organic molecules is probable. Owing to the high degree of dispersion of the gold sol, even when reversibility is observed, its aggregation under these conditions occurs after the passage through the barrier to the near-by potential well, including the process under the influence of univalent electrolytes. In other cases metal sols apparently coagulate virtually irreversibly.

An important further development of the theory of the stability of lyophobic colloids involves its application to a mixture of electrolytes. In view of lack of space, we refer the reader to the relevant literature[114-121].

VI. LANGMUIR'S THERMODYNAMIC CONCEPT OF COACERVATION AND COAGULATION PROCESSES

We shall now consider Langmuir's interesting attempt[122] at a thermodynamic approach to changes in the state of highly disperse colloid systems such as colloidal electrolytes. By analogy with the phase equilibria in molecularly disperse systems, for example, solutions, Langmuir considered temperature, numerical concentration, and osmotic pressure as the thermodynamic parameters of such systems. The expression borrowed from the Debye–Hückel theory of strong electrolytes is used for the osmotic pressure p:

$$p = kT\sum n_i - \frac{e^2\varkappa}{6\varepsilon}\sum_i n_i z_i^2, \quad (86)$$

where n_i is the concentration of ions with a valence z_i. The second term on the right-hand side of the equation expresses the decrease of the osmotic pressure caused by collective electrostatic interaction forces of all the charged particles and ions in which the influence of attraction forces predominates, which accounts for the sign of this term (because $\Sigma n_i z_i^2 > 0$).

Thus Langmuir treats colloid particles as large multicharged ions with a fixed charge. At the same time he considers the limiting case where no ions other than counterions are present in solution. However, Langmuir assumes that, with increase of the concentration of colloid particles, their charge falls owing to the conditions of a constant potential on the surface of the particles. As a result, Langmuir concluded that the dependence of the osmotic pressure on concentration is analogous in form to the van der Waals equation for real gases. From this, it follows immediately that, as the concentration of the sol increases, it may separate into two sols at different concentrations, which are in equilibrium. Langmuir postulates that one can explain in this way not only the coacervation of proteins but also the coagulation of lyophobic sols.

Langmuir's theory was subjected to a serious criticism in the book of Verwey and Overbeek[123], which was not answered. In particular, it was noted that, with increase of the charge of any ion, the applicability of the linearised Debye–Hückel equation is impaired. On the other hand, for the particles of a sol or a colloidal electrolyte, this equation leads to completely incorrect results. When Langmuir's theory is applied to ordinary electrolytes to determine their solubility, the ascending section of the $p(n)$ curve is determined by Born forces and not by the operation of ionic-electrostatic interaction forces.

The following may be added to Verwey and Overbeek's criticism of Langmuir's theory. Coagulation is a process in which a colloid system passes from one state to another under significantly non-equilibrium conditions and is characterised either by the aggregation of particles or by a decreased degree of dispersion as a result of their coalescence. The thermodynamic approach based on the

concentration dependence of the osmotic pressure cannot therefore be adopted for the determination of the rate of coagulation and for predicting its practical feasibility (when the rate is not unduly low).

Calculations on coagulation, according to Smoluchowski and Fuchs, must be based on a procedure taking into account the pair interaction forces between colloid particles approaching one another. In such approach of two particles the distances between the counterions surrounding them and between the counterions and colloid particles do not in any way change in the same proportions as in the phase transitions considered by Langmuir. The deformations of the ionic atmospheres around both particles are determined on the basis of the Boltzmann–Poisson equation taking into account the electrical interaction. In the approach of two identical colloid particles surrounded by ionic atmosphere repulsion is therefore never replaced by attraction.

The difference between the signs of the interaction in Langmuir's theory and in the theory of the pair interaction between particles can be explained by the fact that in the former case the interaction is regarded as a collective effect while in the latter it is a pair effect. The interaction force between particles in the former case is obtained by differentiating the Gibbs free energy of the system, for a constant volume of the dispersion medium, with respect to the concentration (or volume) of the entire system of particles including counterions. The interaction force in the latter case is obtained by the partial differentiation of the free energy of the system with respect to the distance between two isolated particles, assuming that the concentration of the surrounding particles and counterions is unchanged. Thus the difference between the signs of the two effects is not a contradiction. Hence it follows that Langmuir's approach is in principle inapplicable to the development of the theory of the coagulation of colloids. Despite this, Langmuir's work is valuable because he was the first to draw attention to the problem of phase equilibria and transitions in colloid systems. Consequently, it is appropriate to formulate the question of the existence not only of the aggregation equilibrium or equilibrium disperse phase composition, but also of the phase equilibrium, which may break down without a change in the degree of aggregation or dispersion owing to a change in the numerical concentration of particles—an increase in their density.

VII. THE FORMATION AND STABILITY OF PERIODIC COLLOIDAL STRUCTURES†

If one disregards the defects pointed out Verwey and Overbeek, Langmuir's thermodynamic approach can apparently be applied not only to the treatment of coacervation, i.e. the separation of a colloid system into two "phases" with different concentrations, but also to a number of other processes, for example, processes such as the formation of certain periodic colloidal structures (PCS). The question of the conditions governing the formation and stability of PCS is very complex and has been inadequately worked out. We shall therefore confine ourselves to the folowing general considerations without a detailed discussion, the reader being referred to the relevant literature[93,124-127].

†This chapter was written jointly with I. F. Efremov.

The fundamental characteristics of the formation and behaviour of different types of PCS were established as a result of the extension of the DLVO theory to processes involving the conversion of sols, suspensions, and emulsions into gels[128-130]. It was shown that, as a result of the interaction between micro-objects over long distances, different (depending on the conditions) regular structures are generated.

Periodic Colloidal Structures Filling the Entire Volume of the System

Their quasi-crystallinity has been confirmed by numerous experimental data, including direct observations of coexisting hexagonal and cubic lattices in concentrated latexes[131]. In these systems the repulsion forces between the particles, which are stable in relation to direct adhesion to one another, usually exceed the attraction forces[132-134]. Thus "constrained" conditions arise in the system, under which the average distance between the surfaces of the particles is smaller than that corresponding to the second minimum on the potential curve for their pair interaction[124].

The spontaneous transition of individual particles from the secondary to the primary minimum can gradually cause the breakdown of the regularity of the structure (Fig.8) up to the complete disappearance of "crystallinity". However, for very high potential barriers (of the ionic-electrostatic or solvation type), the state of the system approaches equilibrium, which is the reason for the prolonged maintenance of order in it.

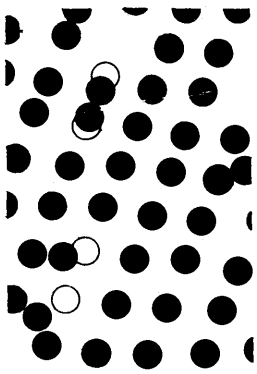


Figure 8. Defects in the periodic lattice of polystyrene particles with a radius of 950 Å caused by the transition of the particles through the potential barrier to the primary minimum.

Periodic Colloidal Structures Filling Part of the Volume of the System

These are tactoids—gel-like deposits. Under appropriate conditions, the local ordered structure in such formations coexists with a "phase" in which the particles are distributed at random, as in an ordinary dispersion medium (a sol or a suspension), but with a definite homogeneous numerical concentration. In some cases this

concentration is not much less than the numerical concentration of the PCS, while in others it is much less and sometimes becomes virtually zero.

The formation of local ordered structures is possible in two cases: when the attraction forces predominate over repulsion forces and when constrained conditions arise.

Owing to the predominance of attraction forces over repulsion forces at long distances and the maintenance of a force (potential) barrier, in the former case the particles may remain fixed for a long time relative to one another owing to the remote potential well. The fixation of micro-objects at the secondary minimum (long-range aggregation) has been observed a comparatively long time ago by numerous investigators and has been confirmed by the results of a large number of studies published recently and undertaken to investigate the influence on long-range aggregation by electrolytes, the size, shape, and concentration of colloid particles, and external electric and magnetic fields, which enhance the attraction forces between the particles [126]. The distribution of particles between the ordered and amorphous "phases" depends on the concentration and valence of ions, the concentration, size, and shape of the particles, the nature of the medium, etc.

The experimental data obtained by various investigators confirm the theoretical conclusions. In particular, the following law holds satisfactorily:

$$nz^{\chi}=\text{const},$$

where n and z are the concentration and valence of the counterions, expressing the influence of electrolytes on the aggregation threshold at the secondary minimum. The theoretical and experimental power exponents χ for both rapid coagulation ($\chi = 6$) and for long-range aggregation ($\chi = 2.5-3.5$) are in good agreement [127].

In the latter case the ordering of the structure takes place under the influence of external, including electrical, forces owing to the appearance of constrained conditions at some place in the stable dispersion, which is associated with the increase of the local concentration of colloid particles. Such PCS include "schiller" layers, gel-like deposits, formed in certain disperse systems, and also cream. In practice, such conditions are generated by the wide-scale application of centrifugal fields to dispersions [135, 136]. To a first approximation, one can assume that these fields do not alter the magnitude of the forces acting between surfaces which have approached one another. The structures arising under these conditions are analogous to the PCS with a limited volume of the medium and accordingly exhibit a ready reversibility; they can serve as model systems in the study of the formation and properties of PCS under constrained conditions.

It is of interest to investigate the distribution of particles between the ordered and disordered "phases" in the field of centrifugal forces as a function of the properties of the system and the field parameters. Concentrated "phases" (for example, electrophoretic coatings) with the required densities and other properties are obtained similarly with the aid of electrical and magnetic fields.

The possibility of equilibrium between a quasi-crystalline "phase" and an "amorphous phase" at a lower concentration has been demonstrated theoretically by Kirkwood [137] and confirmed by the results of the computer experiments of Alder et al. [138] According to these studies, a model system made up of identical solid spheres (or discs), between which there are no long-range forces (attraction or repulsion) of any kind, forms a periodic quasi-crystalline lattice when the volume of the system is half filled. According to Kirkwood's theory, this ordering is a paradoxical consequence of the purely random motion of individual particles. The authors noted that this quasi-crystalline "phase" can exist in equilibrium with the "amorphous phase" at a somewhat lower concentration.

Some investigators have used the purely statistical Kirkwood–Alder approach to explain the formation of quasi-crystalline structures in latexes. Thus aqueous dispersions of polystyrene with a volume fraction of the solid polymer less than 0.4 were found to separate into "phases" in the presence of an electrolyte [139]; in benzene dispersions of poly(methyl methacrylate), which swell appreciably in benzene, such layer formation occurred at a volume fraction of polymer particles of 0.1–0.2. [140] Finally, a highly concentrated polystyrene latex was obtained by the ultrafiltration (under a press) of the initial latex stabilised by surfactants and subsequent addition of large amounts of the electrolyte. At a KCl concentration of approximately 1 M an ordered "phase" with an effective volume fraction of the polymer of approximately 0.5 is formed. It is believed [141] that the results of these experiments confirm the validity of the Kirkwood–Alder theory.

Unfortunately the authors of these in general interesting studies [139–141] characterised a dispersion only to a very slight extent (the potential of the surface of the particles in dispersions with a low concentration of ions, the electrical conductivity of the medium, the degree of swelling of the particles, etc. are not indicated). Nor are there any data showing how the concentration of the disordered "phase" varies with time. A doubt therefore arises as to the reliability of the explanation of the results given by the authors on the assumption that there is no force interaction. Furthermore, in the presence of a lower electrolyte concentration, that of the quasi-crystalline phase diminishes. The authors nevertheless believe it possible to apply the Kirkwood–Alder theory to the systems investigated when the true volume of the particles is replaced by their "effective" volume, which exceeds the former owing to repulsion forces due to diffuse ionic layers.

This cannot be accepted, since the Kirkwood–Alder theory was derived for solid spheres in the absence of repulsion forces with a finite radius of action. Cases where the distances between neighbouring particles significantly exceed the distances indicated by the theory as a consequence of the ionic-electrostatic repulsion should evidently be interpreted in terms of another theory where the structure forming factor is the repulsion forces as well as molecular attraction forces. Such comparatively dilute periodic colloidal structures have been known for a long time [94, 125] and have been observed by the authors [143] themselves. Bernal and Fankuchen [142] observed in an early study, for example, that the average distance between the particles of the tobacco mosaic virus increases steadily with decrease of the electrolyte concentration, which is a consequence of the increasing radius of action of repulsion forces. They assume that in these periodic structures each particle executes an oscillatory Brownian motion about positions in which the repulsion forces, arising from neighbouring particles, are in mutual balance. Evidently particles located at the boundary with another much less concentrated "phase" cannot be in balance if they are acted upon only by repulsion forces from the side of neighbouring particles. The equal force opposing them will expel particles located on the boundary to the outside, i.e. to the less concentrated phase. However, equilibrium is possible if long-range attraction

forces operate together with repulsion forces. Quantitative calculations on conditions for such equilibrium, taking into account the theory of electrostatic repulsion forces and molecular attraction forces, have been described[127]. The separation into phases in the coacervation of sols consisting of rod-like particles, leads to the appearance of an anisotropic phase (tactoids) analogous to nematic liquid crystals. An example is provided by the quasi-crystals of the tobacco mosaic virus[142,144].

A theory of this phenomenon was described by Onsager[145], who also began with the calculation of the osmotic pressure and the chemical potential of the colloid system. This treatment is based on the general expression taken from statistical mechanics:

$$p = kT\frac{\partial \ln B}{\partial V}, \qquad (87)$$

where V is the volume of the system and B is given by

$$B(N, V, T) = \frac{1}{N}\int \exp\left(-\frac{W_N}{kT}\right)\prod_{i=1}^{i=N}(\mathrm{d}q_i); \qquad (88)$$

here N is the number of particles and W_N the potential energy of the interaction of the particles, which depends on their configuration, determined by the generalised coordinates q_i.

In contrast to Langmuir, Onsager considers the case of non-spherical particles, in particular rods and discs. In the calculation of the function B Onsager uses the Mayer–Mayer method[146], neglecting, like Langmuir, the van der Waals forces and also, at the beginning of his exposition, the ionic-electrostatic repulsion forces, but he does take into account the repulsion forces arising on direct contact between the particles. At the end of fairly complex calculations, Onsager found that the system can separate into two stably coexisting "phases": isotropic and anisotropic. At equilibrium the concentration of the latter is higher than that of the former by a factor of 1.34, which is close to the experimental data. For such separation to occur, the volume fraction of the sol particles must be higher than a definite limit where the influence of the effective volume of the particles on the osmotic pressure becomes sufficiently significant. An important result of the Onsager theory is that the greater the deviation of the particle from the isometric shape (for which the effective volume is equal to four times the intrinsic volume of the particles), the lower the volume fraction of the particles in the system for which separation into "phases" is observed. Thus, for rod-like particles, the critical volume fraction, above which the differentiation of an anisotropic phase with oriented particles is observed, is inversely proportional to the ratio of the length of the particles to their diameter. The ability of a sol with extended particles to form tactoids was thus explained.

Later in his communication[145] Onsager takes into account the influence of the ionic-electrostatic repulsion forces, which he neglected at the beginning. For sols with rod-like particles, this leads to the conclusion that, in the calculation of the critical concentration for the onset of coacervation, the effective diameter of the particles must be increased by an amount δ, which is approximately proportional to the thickness of the ionic atmospheres. As a result, the "effective" volume fraction of particles increases to the critical theoretical value for a lower actual volume fraction. This effect, facilitating coacervation in systems with rod-like particles as the electrolyte concentration decreases, has also been observed experimentally.

This effect, discovered by Onsager, should depend, on the one hand, on the influence of the rotational Brownian motion of anisometric particles on the osmotic pressure and, on the other, it should depend on their orientation. Nevertheless, there is no quantitative agreement between the theory and experiment in terms of certain data[147]. Isachara developed the theory for systems with spherical particles[148,149].

It must be emphasised that colloidal quasi-phases, analogous to ordinary phases, constitute an unusual special case. Its manifestation requires primarily the maintenance of approximate monodispersity and certain concentration and temperature ranges. Its occurrence does not constitute a reason for underestimating the fundamental differences between disperse, typically heterogeneous systems, with the characteristic variability of the degree of dispersion and the decisive role of surface phenomena at interfaces, and ordinary single-phase systems.

VIII. MICELLAR SOLUTIONS

The fundamental difference between colloidal and true or molecular solutions noted above does not rule out the existence of semicolloid systems, occupying an intermediate position. These include micellar solutions. They are quite stable thermodynamically and at the same time exhibit a definite degree of dispersion, which can vary as the temperature and composition are altered. The micelles exhibit a certain scatter with respect to the molecular (more correctly micellar) weight, although it is frequently very small. In connection with the existence of micellar solutions, it is appropriate to consider the general problem of the possibility and conditions for the existence of thermodynamically stable disperse systems. This problem has been formulated in the following simplified form[150–153]. It is required to satisfy the conditions for the existence of a minimum in the free energy of a monodisperse system in relation to a virtual change in the latter such that the size of the particles is altered but the monodispersity is maintained. Naturally, this type of equilibrium has nothing in common with the equilibrium of periodic structures. Evidently the required conditions are necessary but not sufficient, since there remains the possibility of a spontaneous breakdown of monodispersity.

One of the conditions isolated by Kachanova et al.[161] is

$$\sigma \ll \frac{\gamma kT}{R^2}, \qquad (89)$$

where σ is the free energy per unit interface between particles with a radius R and the dispersion medium and γ is a numerical coefficient.

The significance of this condition is that, for fairly low values of σ, there is no tendency for the degree of dispersion in the system to decrease during ageing, since the decrease of the free surface energy in such a process is compensated by the increase of entropy. However low (but finite) is the value of σ, condition (89) can hold only if the radius of the particles is smaller than a certain value. The spontaneous dispersion of an arbitrarily coarse phase can therefore occur only as a result of the separation from the latter of sufficiently small particles, which can occur, in particular, as stated by Rebinder and coworkers[152,153], owing to internal stresses, the liberation of the energy of which makes it possible to overcome the activation energy barrier, which prevents such "colloidal dissolution".

However, it has been noted[151,154] that condition (89) must be supplemented by another condition, which, in contrast to the first, might hinder an unlimited increase of the degree of dispersion up to the formation of a true solution. This condition has been formulated[154] as follows:

$$-\frac{\partial \ln \sigma}{\partial \ln R} > 2. \qquad (90)$$

We shall consider the problem of the kind of systems for which this condition can hold. According to Shcherbakov[155] (see also Tolman[156]), the dependence of the free surface energy on the radius of spherical particles for one-component systems satisfies the relation

$$-\frac{\partial \ln \sigma}{\partial \ln R} = -1, \qquad (91)$$

which is incompatible with condition (90). At the same time this incompatibility with condition (90) may not obtain for three reasons. Firstly, condition (91) is valid only in the asymptotic case where $R \to \infty$. Secondly, both conditions may be modified in multicomponent systems. Thirdly, condition (91) has been derived for molecules interacting on the basis of central forces and is presumably inapplicable to diphilic molecules (for example, the molecules of soaps), the opposite ends of which exhibit affinity for phases of different polarity.

It is noteworthy that the derivation of equilibrium conditions was not accompanied by the analysis of the problem of the particular systems for which these conditions can be realised. This question is undoubtedly very difficult to resolve but is also the most important. We shall therefore now return to experimental results.

Only two types of fully (thermodynamically) stable colloidally disperse systems have now been firmly established—critical emulsions and micellar solutions. The theory of critical emulsions was first described by Volmer[157-159] and was improved by other workers[150,160,161]. However, the instability of the droplets of such emulsions has more in common with associated species in polar liquids than with stable colloid particles. Critical emulsions can therefore be hardly classified as colloid or even semicolloid systems.

Micellar solutions, to which soap solutions‡ belong, for example, are of great practical importance, being extremely varied and usually consisting of two or more components, at least one of which exhibits a high surface activity.

The literature devoted to micellar solutions is extremely extensive and contains many theoretical studies. In this review we are unable to discuss them and we shall confine ourselves solely to remarks of a general nature on the problem of the stability of disperse systems. Micelles are known to have different shapes, usually spherical, cylindrical, or lamellar[162]. The surface of cylindrical micelles is non-isotropic (has no circular symmetry) and the properties of the directions along the generatrices of the cylinder differ from those of the directions along the tangents to the perimeters of the normal sections. This can be explained in many instances by an orientation of the dipolar molecules on the surface such that the projection of the dipole moment of the molecules onto the surface of the micelle§ coincides with one of these two directions. For highly extended micelles, these projections should be tangential to the perimeters of sections of the cylindrical surface, according to the conditions for the free energy minimum[164], forming closed chains, and for this reason the external electrostatic field is extremely weak. At the same time if it is assumed by analogy with formula (90) that the formation of a micellar solution from a molecular solution is associated with the dependence of σ on the surface curvature, then, in order to apply Eqn.(91) to cylindrical micelles, it must be generalised by introducing the derivatives of the free interfacial energy with respect to the principal radii of surface curvature, one of which is zero and the other is equal to $1/r$ (r is the radius of the micelle).

IX. THE FORMATION AND STABILITY OF LIQUID FILMS

It is well known that many micellar solutions form liquid-crystal, for example smectic, phases in a particular range of concentrations and temperatures[167,168]. Such systems resemble a layer cake (Fig. 9). Some layers (*W*) consist of the polar, in most cases aqueous, phase, while others (*C*) consist of the hydrocarbon phase; at the interface there are layers of diphilic surface-active molecules oriented with the polar end towards the aqueous phase. The layers of hydrocarbon phase are frequently absent and only oriented bimolecular layers of diphilic molecules (analogous to lipid membranes) are located between adjoining layers of the aqueous phase. The system as a whole has a one-dimensional periodic structure.

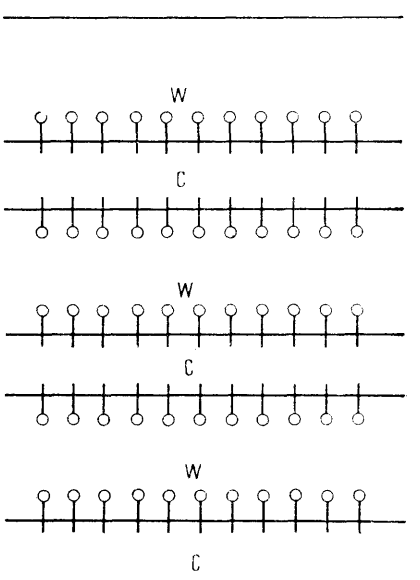


Figure 9. Schematic illustration of a one-dimensional periodic micellar solution.

‡Attention has recently been concentrated on stable microemulsions. They are in essence a variety of micellar solutions.

§The existence of this type of inclination of dipole monolayers is well known and in addition follows from the electro-optical studies of Tolstoi and Spartakov[163,164]; the theory of this phenomenon has been described by Deryagin and Shulepov[165,166].

The same solutions are capable of forming stable thin symmetrical films of the type of foam[169], whose thickness at equilibrium differs, however, from the repeat period of the above liquid-crystal structures even when the latter do not contain non-polar layers[170].

Evidently the task of the theory is to explain the cause of the formation and stability of both smectic structures of this kind and of isolated symmetrical films. The thermodynamic stability of free films, ensured by equilibrium between capillary suction and the wedging pressure, was first demonstrated by Deryagin and Titievskaya[171,172]. In the first place the problem arises of the nature of the repulsion forces which balance the van der Waals component of the wedging pressure, tending to make the layers thinner, and ensure thereby an equilibrium polymolecular thickness of the aqueous layers. The equilibrium thickness of the so-called primary free films, observed at low electrolyte concentrations, is largely determined by ionic-electrostatic repulsion forces and amounts to several hundreds of Angstroms. The primary films are metastable and under certain conditions are either ruptured or are abruptly converted into secondary or Perrin films. Under certain conditions both types of behaviour can coexist, being separated by an interface (in the form of a circle or its arc) at which the thickness of the film changes abruptly[174,175,195]. The secondary films observed at high electrolyte concentrations, at which the electrostatic component of the wedging pressure is infective, have a thickness of approximately 20–60 Å.[173-178]

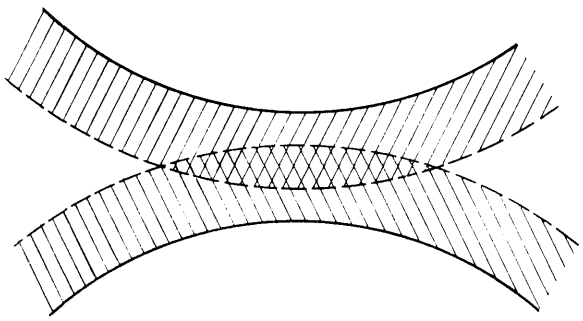


Figure 10. Schematic illustration of the overlap of surface layers.

In the light of the results of a series of experimental studies[179-182], one of the causes of aqueous layers retaining their thickness may be the structural component of the wedging pressure. In essence the same idea was put forward by Clunie et al.[183]. The origin of this component is as follows. The water layers at the interface between the aqueous phase and the hydrophilic surface or hydrophilic functional groups of the molecules adsorbed at the interface acquire under the influence of the latter a structure different from that in the bulk phase. The difference may consist, for example, in a modification of the network of hydrogen bonds and also in the polarisation of the molecular dipoles, which should be promoted by the oriented adsorption of diphilic molecules[184,185]. When the water layer becomes thinner, the boundary layers belonging to both surface layers may overlap (Fig. 10). This overlap should entail the disruption of the unusual structure of the peripheral parts of the boundary layers which leads to an increase in the amount of water with the properties of the bulk phase. This process initiates a change in the free energy of the system, which is inevitably associated with the generation of the wedging pressure. The role of the structural characteristics and the stability of secondary films is confirmed by the fact that aqueous solutions of surfactants, stabilising these films, are capable for forming liquid-crystal phases.

The secondary films are disrupted by the formation of a point break, or spontaneously, or under the influence of a spark, or on passing from α-rays.[169]

The theory of the rupture of secondary films, in the simplest case where the process is unaccompanied by local changes in thickness and takes place in only two dimensions, was developed by Gutop and Deryagin[197]. It is noteworthy that the assumption of a purely two-dimensional flow of all sections of the film during nucleation (the formation of a nuclear hole) constitutes a fairly rough first approximation. This approximation is altogether inapplicable to the primary thicker films, which greatly complicates the construction of a rigorous theory of their rupture or conversion into secondary films.

Theories permitting the calculation of the critical thicknesses and other conditions for the spontaneous conversion of primary films into secondary films have been developed in a number of studies[198-203], but these cannot be described here.

One of the important tasks of the theory of the stability of disperse systems consists in the development of a quantitative theory of the structural component of the wedging pressure. The main difficulty in this task is associated with the fact that the nature of the structure of water, even in the bulk phase, is controversial and cannot be regarded as reliably established.

Another example of a quasi-disperse system with a rigorously periodic structure in one direction is montmorillonite in the state of intracrystalline swelling[186]. The mechanism of the first stage of the swelling process, where the aqueous layer between elementary crystalline network layers, which has a thickness of the order of 10 Å, corresponding to a few molecular layers, may be compared with the formation of liquid-crystal smectic phases accompanied by the appearance of the components of the wedging pressure. At a low ionic strength of the surrounding solution, the second stage of the swelling process, referred to as osmotic, begins. Under the influence of the ionic-electrostatic component of the wedging pressure, aqueous layers can then be formed with an equilibrium thickness ranging from 10–20 to 300 Å, depending on the ionic strength[186]. Measurements of their thickness by X-ray diffraction may serve as a test (in terms of a model) of the theory of interaction of charged surfaces in electrolyte solutions and of the theory of the formation of colloid layer structures, including "schiller" layers.

For small thicknesses, the collective nature of the van der Waals interactions in closely spaced elementary crystalline layers (scales) constitutes in essence a complication, while for large thicknesses and low wedging pressures a complication arises from the mechanical jamming of the scales by the end faces of the adhering neighbouring scales[187]. The study of the state of equilibrium of free symmetrical films, first observed and investigated mainly by the present author and his coworkers[171-178], therefore has many advantages for model investigations. In this case it is possible to vary

the specified wedging pressure and to measure the thicknesses of the film and the aqueous layer by optical methods. A number of experimental studies made it possible to obtain a quantitative conformation of the theory of the electrostatic and van der Waals components of the cleaving pressure [189].

The most complete confirmation of this theory was obtained by Deryagin, Voropaeva, and Kabanov, who used crossed metallic wires in electrolyte solutions, whose potential could be varied by polarisation, as models of the interaction of particles in metal sols [190-194]. Apart from confirming the above theory, these measurements made it possible to determine the van der Waals interaction constant. At the same time lower values of the wedging pressure at the zero charge point and at high (of the order of several moles per litre) concentrations, which are not covered by the theory, were observed. Thus the theory of the wedging pressure of thin layers, which permits the calculation of their equilibrium thicknesses, has been confirmed in certain cases.

X. INTERACTION OF NON-IDENTICAL SURFACES

A theoretical treatment of the stability of disperse systems and thin films was described above for the interaction of surfaces of identical nature and having the same charge. The interaction of surfaces of different kinds and bearing different charges has been examined [204,205]. The following are the most significant theoretical conclusions.

The electrical component of the wedging pressure for surfaces bearing opposite charges is negative for all distances, i.e. corresponds to attraction. Surfaces charged to different potentials of the same sign alter the sign of the interaction from repulsion at long distances to attraction at short distances. The force barrier to mutual approach depends only on the potential of the surface which is charged to the lower potential. The van der Waals component of the wedging pressure of layers between bodies of different kinds may be positive (this conclusion was later confirmed [206,207] within the framework of the macroscopic theory of intermolecular forces). If the surfaces are simultaneously charged to very high potentials of different sign, then the inverse Hardy–Schulze rule is valid: the rapid coagulation threshold occurs as the concentration is decreased to a value inversely proportional to the ionic charge raised to the sixth power (for a symmetrical electrolyte).

This theory of heterocoagulation was developed further in other studies [208,209]. The case of surfaces with specified surface charge densities has also been examined [210-212]. Devereux and de Bruyn [213] published tables for the electrical components of the wedging pressure. Smilga [214] examined the case of an arbitrary mixture of electrolytes. The case of low potentials, examined initially by Deryagin and Levich [215], was later considered in greater detail [216,217].

The theory has received experimental confirmation in a number of studies; in particular, the inversion of the Hardy–Schulze rule was confirmed by Chernoberezhskii [218]. A rigorous quantitative comparison of experiment with theory is hindered mainly by the difficulty of determining the effective surface potential of the particles. Model experiments in which a study was made of the conditions for the mutual adhesion of two mercury drops polarised to different potentials [219, 220] as well as mercury and glass drops [221-223] are of interest in this respect. The mutual adhesion of mercury drops in a hydrocarbon medium was investigated by Srenge and Sonntag [224]. The wedging pressure of the electrolyte layer between the glass and the polarised mercury drop has also been investigated [225]. The theory of heterocoagulation was tested and confirmed [226,227] also by observing the adhesion of disperse particles to a rotating disc. It must be emphasised that heterocoagulation constitutes a wider range of phenomena than homocoagulation, which is its special case. Heterocoagulation constitutes the basis of such major problems as those of flotation [228-231], the purification of water in filters [232], dyeing, the adhesion of biological cells, etc. [233] The development, testing, and application of the heterocoagulation theory therefore undoubtedly merit further attention and efforts (see also Prieve and Ruckenstein [234]).

XI. CONCLUSION

The present review has shown that the theory of the stability of disperse systems and thin films is of the greatest importance for colloid science and for many fields involving surface phenomena. Despite the enormous literature on this problem, published during forty years, there is still much room for its further development and investigation, particularly as regards a quantitative test of the theory. It is also necessary to approach more rigorously the very definition of the concept of the stability of colloids, differentiating strictly its different varieties and aspects and avoiding a one-sided approach.

It must be emphasised that the development of the theory of the stability of colloids and the wedging pressure as its basis also led to progress in solving the purely physical problem of intermolecular forces and the electrochemical problem of the ionic double layer. This stimulating influence of the science of the stability of colloids merits its more detailed consideration in conclusion.

Although it had been known earlier that the molecular interaction in condensed media is non-additive, nevertheless up to 1955 it was generally accepted, following de Boer, Bradley, and Hamaker, that the degree of interaction between macro-objects should be found by integrating pair dispersion interactions with respect to their volumes. The first limitation of this procedure was pointed out by Casimir [235], who developed a more accurate quantum theory of dispersion interactions taking into account the finite rate of propagation of electromagnetic vibrations. As a result, molecular attraction over distances significantly greater than the characteristic length, where the electromagnetic lag is already fully manifested, begins to weaken more rapidly by a single power of the distance.

Casimir was also the first [236] to describe an example of a macroscopic theory of van der Waals forces, having devised it for the case of two metallic plates separated by distances over which the electromagnetic lag is fully manifested. The first study which demonstrated experimentally the inapplicability of the Hamaker method to the calculation of the attraction of macro-objects was that of Deryagin and Abrikosova [237-241]. The force of attraction of a glass (or quartz) lens to a similar plate was first correctly measured in their investigation as a function of the gap separating them¶. It was found that the experimental

¶ Owing to the incomplete elimination of random electrical charges, the measurements of Overbeek and Sparnay [242] published simultaneously were erroneous. They yielded attraction forces exceeding by a factor of thousands the true molecular attraction and were even greater than the value yielded by calculation without allowance for the electromagnetic lag.

attraction force in the range of gaps 500–5000 Å is much weaker than the value obtained when Hamaker's formula is applied. This result led Lifshits[243] to develop a macroscopic theory of van der Waals forces acting between macro-objects of any kind.

The experimental data agreed, within the limits of the error of the measurements, with data calculated from the formulae for the complete manifestation of the electromagnetic lag. Subsequently Deryagin and Abrikosova carried out measurements on another object (the quartz–chromium pair and the NaBr–NaI mixed crystal) and in all cases agreement between theory and experiment was demonstrated[244,245]. An analogous conclusion was arrived at later by experimenters using other methods. Recently it has been possible to extend the treatment also to the range of gaps for which the limiting laws neglecting the electromagnetic gap are valid[246,247]. In particular, measurements have been made for the first time on the molecular attraction between two metallic objects[248,249].

The reader is referred to reviews[250,277] of experimental studies and further theoretical developments, while here the following remarks will be made.

Dzyaloshinskii et al.[251] extended the theory to the case where the interacting plates are immersed in any medium, which is of particular interest for colloid science. Here it is important that the general formulae make it possible to calculate beforehand the interaction force, provided that the characteristic regions of the optical absorption spectra of both bodies and the medium are known. This possibility has been tested experimentally in many instances and is exceptionally valuable for the theory of the stability of disperse systems.

Recent studies, designed to develop further the theory of the electrical double layer (DL), took into account the influence of the intrinsic volume of ions and pair correlations on the DL structure[252], of the polarisation of DL on electrophoresis and diffusiophoresis[253], of adsorbed ions on the structure and polarisability of DL [254]; the problems of the discrete nature of DL [255], of the determination of the surface potential of spherical particles,[256] and of the comparison of the constant surface potential and constant surface charge conditions in the DLVO theory[257] have been examined. Furthermore, the results of studies of the interaction of DL of charged surfaces have been published: for a solution of a mixture of electrolytes[258], for planar particles in concentrated dispersions with a dispersion medium having a low dielectric constant[260], for constant surface charges[49,263], and for a constant potential of one surface and a constant charge of another[264,266].

In a number of studies an interesting attempt has been made at a unified treatment of the interaction energy (van der Waals attraction and electrostatic repulsion) of charged surfaces[267,268]; the low-frequency electromagnetic fluctuations and the statistical charge distribution between two plates have been examined jointly[269,270] and account has been taken of the influence of the dielectric constant of the medium on the energy of an ion near the interface[271]. The method of images has been used[272] to calculate the interaction energy of two different dielectrics separated by a layer of a third dielectric. The interaction of surfaces with energetic and geometrical inhomogeneities has been examined[273,274]. Reviews of the literature on the surface forces in disperse systems have been published[275–278]. The stability of black hydrocarbon films has been comprehensively examined in the monograph by Kruglyakov and Rovin[279]. Various questions of the stability of colloids have been discussed[280]. The wedging pressure of liquid-crystal films has been considered[281].

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The Influence of Hydrogen Bonds and Ionic Interactions on the Properties of Carboxyl-containing Copolymers and Ionomers Based on Them

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The changes in the properties of copolymers as a function of the introduction of units with carboxy- and salt groups into the macrochain are examined. Attention is concentrated on the analysis of the results of the study of copolymers in the acid and ionomeric forms in solutions. The decisive influence of ionic interactions on the properties of ionomers in bulk and on their hydrodynamic and conformational characteristics is demonstrated. The difference between hydrogen and ionic bonds in the sense of their effects both on the primary ordering of macromolecules within the chains in copolymers of the types indicated and on the interchain interaction processes is emphasised.
The bibliography includes 163 references.

CONTENTS

I. Introduction 389
II. The influence of hydrogen bonds on certain properties of carboxyl-containing copolymers in bulk 389
III. Manifestation of the specific interaction between carboxy-groups of copolymers in solutions 390
IV. The influence of ionic interactions on the properties of monomers in bulk 393
V. The properties of solutions of copolymers with ionogenic salt groups 394

I. INTRODUCTION

One of the achievements in the regulation of the properties of polymers by the modification of their structure is the synthesis of ionomers. The term "ionomers" was first ascribed to ternary copolymers of ethylene with acrylic acids and their salts[1-6]; at the present time it is also used for other copolymers with ionogenic salt groups. The effective operational and technical properties of ionomers were already reported in the first studies, which attracted to them the continuous attention of specialists in many countries. The results of large-scale studies indicate some common features of ionomers of a wide variety of classes due primarily to the ionic and polar interactions in the macromolecular matrix.

Apart from the dispersion of dipole type interactions usual for all polymers, in the solid state ionomer macromolecules are also linked by ionic bonds, which are the strongest among those known; account must also be taken of the presence of hydrogen bonds between COOH groups. In dilute solutions the conformational characteristics of ionomers are in many respects determined by the same types of specific interactions, but this time at an intramolecular level. The differential approach to the assessment of these interactions and the determination of the dominant ones will permit a comparison of the properties of carboxyl-containing copolymers (CCC) in an acid form and copolymers with partial or complete neutralisation of the carboxy-groups by metal ions (ionomers). Since the properties of ionomers in the solid state are being investigated very vigorously at the present time and a number of reviews[7-16] deal very completely with the situation in this field, in the present review attention is concentrated on the result of the study of the CCC and ionomers in solution.

II. THE INFLUENCE OF HYDROGEN BONDS ON CERTAIN PROPERTIES OF CARBOXYL-CONTAINING COPOLYMERS IN BULK

The specific properties of solid carboxyl-containing copolymers and their solutions are to a large extent determined by the ability of the CCC to form hydrogen bonds which give rise to additional stronger contacts at intramolecular and intermolecular levels. The presence of an extensive system of such contacts leads to the appearance in solid CCC of a series of clear-cut effects. The characteristics of the formation and function of hydrogen bonds and the effects induced by them are being investigated by infrared spectroscopic[17-31] and calorimetric[18-20,23,25,31] methods; valuable information is provided by the study of the thermomechanical[18-20,23], viscoelastic[32,33], sorption[28,34,35], and other properties of the CCC.

The vast majority of the carboxy-groups in CCC are linked via hydrogen bonds to the dimeric complexes; the stretching vibration bands of the $>C=O$ groups at 1695 to 1705 cm^{-1} [17,20,21,23,25,29] and the 940 cm^{-1} band, attributed to the migrations of the out-of-plane OH group in the dimer[19,20], correspond to them. Below the glass point T_g, where there is no segmental motion of the chains, the intensity of the bands due to free carboxy-groups (1740 to 1750 cm^{-1}) is extremely insignificant[17,20,21,23,25,29], which indicates a low concentration of such groups in CCC. However, with increase in temperature there is some increase of the intensity of the free carboxyl band, which is particularly noteable near T_g.[17,23,28,29] The dissociation of hydrogen bonds in the styrene–methacrylic acid (MAA) copolymer (85:15) at 120°C leads to the appearance of an inflection in the curves describing the temperature variation of the intensity of the 1745 and 1700 cm^{-1} bands; this inflection corresponds to the glass point, which has been recorded at 120°C also by differential thermal analysis and by dynamic mechanical measurements[23].

The intial fraction of free COOH groups (α) in CCC is appreciably lower than after the heating–cooling cycle: in the range of temperatures above T_g the parameter α assumes its equilibrium value, which persists when the specimen is cooled[29]. The quenching of the structure thus formed leads to a closer packing of the macromolecules (an increase of density) of the hydrogen-bonded copolymer compared with the unannealed specimen[34,36].

The rupture of the main bulk of hydrogen bonds after the attainment of T_g can hardly be regarded solely as a consequence of the thermal lability of the corresponding cross links, since in this case one would have observed a steady shift of T_g towards higher temperatures with increasing content of COOH groups in the copolymer[17-20,23,29,37]. The

dissociation of hydrogen bridge bonds is apparently promoted, apart from temperature as such, also by the increased thermal motion of the chains. This apparently explains the dependence of the equilibrium constant for the formation of hydrogen bonds on the concentration of carboxyl-containing units in the copolymer[29]. The hypothesis that hydrogen bonds can be broken as a result of the active motion of macrochains is consistent with experimental data[25,28] concerning the stabilisation of the network of hydrogen bonds between carboxy-groups in partly neutralised CCC specimens (ionomers), because the appearance of strong hydrogen bonds increases the mobility of the chains. The fixed position of carboxylate ions in ionomers makes the relative intensity of the 1723 cm^{-1} absorption band (stretching vibrations of carboxy-groups involved in hydrogen bonds with carboxylate ions) unchanged even at temperatures above T_g.[28]

The observed changes in the T_g of CCC as a function of the number and type of hydrogen bonds are consistent with the view according to which certain transitions (of the T_g type) are interpreted[38] simply as a consequence of the disappearance of the different types of intermolecular (secondary) bonds in the solid polymer specimen.

Hydrogen bonds make an appreciable contribution to the enthalpy of the vitreous state, which is proportional to the content of carboxyl-containing units in the polymer[18]. The heat of dimerisation of carboxy-groups found for various CCC varies from 7.32 to 11.6 kcal $mole^{-1}$,[17,19-21,23,29], i.e. is very close to the value characteristic of low-molecular-weight compounds with COOH groups in non-polar solvents[39]. With increase of the degree of neutralisation of carboxy-groups in CCC, the enthalpy of the residual intermolecular hydrogen bonds increases[25] as a result of their strengthening.

The degree of crystallinity of polyethylene decreases after the introduction of acrylic acid units in consequence of the formation of hydrogen bridge bonds[19,20,21,40]. The crystallinity of such copolymers decreases linearly with increasing content of the acid and reaches zero when the content of acid unit is more than 8–9 mole %.[4,31] The dimerisation of carboxy-groups proceeds only in amorphous parts of the copolymer and the bulky acid groups are thereby excluded from the crystal lattice of the polyethylene[19,20,31]. This is also promoted by the tendency towards spontaneous aggregation of COOH groups in systems of this kind[32]. A certain incompatibility of hydrocarbon units and acrylic acid units, due to thermodynamic factors which is intensified owing to the presence of hydrogen bonds, is manifested to the greatest extent in graft copolymers. This has been shown for polypropylene with grafted polyacrylic acid chains in a study[41] where the presence of two phases was detected with the aid of transmission and scanning electron microscopy, indicating the microheterogeneity of the copolymer structure.

The presence of an extensive network of hydrogen bonds hinders the diffusion of solvent vapour into the bulk of the methyl methacrylate (MMA)–MAA copolymer, such hindrance to diffusion increasing with increase of the content of MAA units in the copolymer, i.e. with increasing density of the hydrogen bond network[34,35]. Analysis of the solvent sorption and desorption pattern and the observed distinct hysteresis demonstrate a redistribution of hydrogen bonds, an appreciable rearrangement of the steric structure of the network, and a change in the polymer–solvent interaction after the attainment of a certain degree of swelling of the polymer. Annealing of the specimens decreases the sorption capacity and causes the disappearance of a whole kinetic region of the sorption isotherms, which is regarded[34] as a critcal effect. The sorption characteristics of CCC depend significantly on the type of solvent–on its ability to compete in the formation of hydrogen bonds[28].

The decrease of swelling in benzene of the graft copolymers of natural rubber with acrylic polymers of methacrylic acid with increasing degree of grafting can apparently also be regarded as evidence for the formation in such copolymers of additional interchain contacts via hydrogen bonds; this tendency towards a decrease of swelling is most pronounced in copolymers with methacrylic acid[42]. The different contributions of COOH groups to the formation of hydrogen bonds as a function of the nature of the acid has also been observed (by infrared spectroscopy) in graft copolymers of starch with acrylic and methacrylic acids[27]. The difference between these acids is also manifested by the fact that the increase of T_g is more pronounced in the graft copolymer of cellulose with methacrylic acid compared with the copolymer with acrylic acid[43].

Although both intramolecular and intermolecular hydrogen bonds can be formed simultaneously in solid CCC, in some cases the interpretation of experimental data leads to the conclusion that interchain cross links are formed preferentially[19,21,23], while in others account is taken mainly of the presence of intramolecular dimeric complexes[17,24].

III. MANIFESTATION OF THE SPECIFIC INTERACTION BETWEEN THE CARBOXY-GROUPS OF COPOLYMERS IN SOLUTION

When we proceed from the consideration of solid carboxyl-containing copolymers to their dilute solution, it is possible to estimate the properties of an isolated macromolecule due to the presence of hydrogen bonds within a given chain only. These bonds can be formed between the carboxy-groups of the same macrochain, between a carboxy-group and another monomeric chain containing a hydrogen bond acceptor (for example in MMA copolymers with MAA), and also between a carboxy-group in the chain and a solvent molecule. However, interchain interactions also begin to be manifested in concentrated solutions.

The formation of intramolecular hydrogen bonds of the polymer–polymer type is not characteristic of polymeric acids, because they dissolve mainly in protic solvents (water, alcohols, and their mixtures). All these solvents ionise the carboxy-groups of the macrochain and in addition they can themselves form hydrogen bonds of the polymer–solvent type. The presence of a single C=O stretching vibration band at 1710 cm^{-1} in the infrared spectrum of the initial polyacrylic acid solution indicates a single type of hydrogen bonds in this system, namely COOH–H_2O bonds[44]. However, in an aqueous alcoholic solution of polymethacrylic acid infrared spectroscopy reveals the appearance of hydrogen bonds within the chains[45].

For CCC, it is possible to use organic solvents with a wide range of polarities and donor–acceptor capacities. By varying the composition of the solvent and the concentration of the polymer in the latter, it is possible to convert hydrogen bonds of one type into another, and thereby achieve a specific influence on the structure of CCC in solution. The presence of hydrogen bonds of all types alters the hydrodynamic characteristics of the CCC; the intensity of their formation is therefore usually inferred from viscometric data, which, together with the results of the study of CCC in solution by other methods, can yield detailed

information about the mechanism of the formation and dissociation of these bonds and about the extent to which they influence the conformational characteristics of CCC macromolecules.

The problem of the possible cross-linking of an isolated macromolecule has been considered theoretically by Kuhn and Balmer[46], who concluded that, when the ring intramolecular bonds are formed, the size of the macrocoil should diminish. Experimental data for the hydrodynamic properties of CCC having hydrogen bonds within the chain confirms this conclusion. MMA–MAA copolymers in which the MAA units are capable of forming stronger contacts, by virtue of the formation of hydrogen bonds, with all other units are interesting in this respect[47-61]; it has proved possible to regulate the effective density of such contacts by altering either the solvent or the relative content of MAA units in the copolymer. It has been shown for MMA–MAA copolymers[47-61] that selective interactions within the chains occur in dilute solutions in consequence of the formation of hydrogen bonds of the polymer–polymer type, which lead to additional contraction of the polymer coil in "inert" solvents (hydrocarbons, halogenated hydrocarbons, and other solvents, which cannot break the hydrogen bonds in the copolymer or which exhibit a very weak capacity for their formation with the carboxy-groups of CCC). In such solvents the macromolecules of the MMA–MAA copolymer undergo internal "vulcanisation" owing to the formation of a network of hydrogen bonds; because of these bonds, the points of contact involving groups which are remote in terms of their positions along the chain proved to be rigidly fixed: the so-called "frozen" conformation arises.

The disruption of the system of such contacts and transition to the state of the usual flexible statistical coil occur when a small amount (several per cent) of a substance actively competing for hydrogen bonds, for example dimethylformamide (DMF), is introduced into the inert solvent–copolymer system. This transition is indicated by the sharp (abrupt) changes in the hydrodynamic characteristics and conformations of the copolymer macromolecules. Since the thermodynamic quality of the solvent at a low DMF concentration in the latter hardly changes, all the effects observed following the addition of DMF are due to a change in the nature of the hydrogen bonds (hydrogen bonds within the chain of the polymer–polymer type are fully converted into bonds of the polymer–solvent type). This indicates an unambiguous correlation between the experimental parameters {particularly $[\eta]$} and the probability of the formation of stable contacts within the chain via hydrogen bonds.

The study of dilute solutions of MMA–MAA copolymers under the conditions of maximum formation of hydrogen bonds of the polymer–polymer type within the chains and when these bonds are broken by the addition of competing substances has shown that the values of $[\eta]$ for the copolymers increase after the introduction of competing substances by a factor of 2–5 and reach the intrinsic viscosities of poly(methyl methacrylate) with the same degree of polymerisation[51-54] or approach the values of $[\eta]$ of the copolymer in solvents where the formation of hydrogen bonds of the polymer–polymer type is impossible[58,60]. The equality of the values of $[\eta]$ and of the Huggins constant for the MMA–MAA copolymer and poly(methyl methacrylate) in a dichloroethane–DMF mixture indicates the similarity of the conformations of the MMA homopolymer macromolecules and the macromolecules of its copolymer with a low MAA content when the internal macrorings in the latter are liquidated[54].

It is significant that, when the hydrogen bonds within the chains are broken, the type of hydrodynamic homology also changes. For the MMA–MAA copolymer (with 7.6% of MAA) in dichloroethane, $[\eta] \propto M^{0.66}$, whereas following the addition of 5% of DMF the power exponent a increases to 0.87, i.e. becomes almost equal to the power exponent in dioxan ($a = 0.86$).[58,60] The intrinsic viscosity of a copolymer with a high content of MAA units (34%) in acetone is almost independent of the molecular weight (a is close to zero).[55,56,58,59] It is suggested that the copolymer macromolecule in acetone has the conformation of a quasi continuous coil highly "cross-linked" by hydrogen bonds, whose rupture as a result of the addition of DMF leads to an increase of a to 0.26.[59] The results illustrate the marked dependence of the conformation of the coil on the nature of the hydrogen bonds.

The efficiency of the formation of contacts via hydrogen bonds is determined primarily by the number of MAA units in the copolymer macromolecule and depends thus both on the composition of the copolymer and on the degree of its polymerisation[62,63]. In consequence of this there is (for a given solvent) a progressive "contraction" of the MMA-MAA copolymer coils as the molecular weight and the MAA content increase[53]. The critical DMF concentration at which the rupture of the network of hydrogen bonds within the chain occurs and $[\eta]$ of the copolymer approaches the value for poly(methyl methacrylate) depends only on the MAA content in the copolymer and is independent of its molecular weight. The contraction of coils via hydrogen bonding is therefore proportional to the number of MAA units in the copolymer and inversely proportional to the DMF concentration in the solvent[57,61].

Other conditions being equal, the efficiency of the formation of hydrogen bonds is also determined by the way in which the units are distributed, i.e. by the microstructure of the copolymer chain[64]. An appreciable difference has been observed between MMA–MAA copolymers having the same composition but obtained in different ways: by the hydrolysis of poly(methyl methacrylate) (statistical distribution of MAA units) or by radical copolymerisation (deviation from a rigorous statistical distribution because MAA units are grouped into diads, triads, etc. to a large extent). In the former case the contraction of coils is more pronounced owing to the greater density of cross linking via hydrogen bonds[57,61,64].

Since the contraction of the CCC macrocoil depends on the degree of polymerisation, the shape of the coils is to a large extent determined by the molecular weight. Strictly speaking even fractions of CCC with a homogeneous composition cannot be regarded as a polymer-homologous series under the conditions of the manifestation of selective interactions within the chain, because the ratio of the dimeric and monomeric forms of the carboxy-groups is determined (other conditions being equal) by the molecular weight of the fraction. In other words one can assume that the fractions, as it were, differ in composition. In this case the more effective formation of hydrogen bonds with increasing molecular weight will promote an anomalous decrease of the power exponent a in the equation $[\eta] = KM^a$; the rupture of hydrogen bonds within the chain owing to the addition of small amounts of a proton acceptor restores the normal value of the exponent. The above changes in a cannot be accounted for by an improvement or impairment of the thermodynamic quality of the solvent. One must therefore take into account the conventional nature of the results of the estimation of the parameters of equations of the Mark–Kuhn–Houwink type (for any hydrodynamic properties) and the unperturbed dimensions

of the CCC obtained by the Stockmayer–Fixman method when selective interactions within the copolymer chain take place[57,61].

Apart from the MMA–MAA copolymers, the presence of cross-links within the chain via hydrogen bonding and their influence on the hydrodynamic characteristics have been established also for other CCC of different compositions based on acrylic[58,65–72] and methacrylic[71,73–75] acids as well as monobutyl itaconate[76–80]. Different inert solvents (toluene, xylene, chlorobenzene, dichloroethane, carbon tetrachloride, bromoform, etc.) were used in the investigation; apart from DMF, other compounds capable of forming hydrogen bonds of the type polymer–solvent (acetic and methacrylic acids, methanol, dioxan, tetrahydrofuran, dimethyl sulphoxide, amines etc.) can also be used as competing additives. The experimental data obtained do not conflict with relations established for MMA–MAA copolymers, although in each specific case particular features of the test system can be manifested. This is associated primarily with the proton-accepting activity of the second component of the solvent, i.e. with its ability to compete with the polymer units in the formation of hydrogen bonds. On the other hand, the mechanism of the dissociation of the hydrogen bonds within the chain is apparently in all cases similar and is determined mainly by the preferential solvation of the carboxy-group by the competing additives.

In contrast to MMA–MAA copolymers, a characteristic feature of which is the formation of two types of hydrogen bonds within the chains, the copolymers of styrene and acrylic acid make it possible to investigate in the "purest" form the hydrogen bonds between the carboxy-group, although the presence of a weak hydrogen bond between the COOH group and the π electrons of the benzene ring has also been observed for systems of this kind[71]. A study of the copolymers of 4-vinylbenzoic (I), acrylic (II), and methacrylic (III) acids with styrene (IV) in carbon tetrachloride has shown that under these conditions the number of bonds of this type increases in the sequence of copolymers (I) – (IV) < (II) – (IV) < (III) – (IV).[71]

Apart from the effect of competing additive properties a study was also made of the effect of temperature on the intramolecular cross-links due to hydrogen bonds in CCC in inert solvents. It has been established that the intrinsic viscosity (which in the given case can be regarded as a measure of the effectiveness of various contacts between carboxy-groups within the chain) remains virtually unchanged over a wide temperature range up to 70 to 110°C; [53,54,58,60,73,80] nor is there any change in the Huggins constant. The constancy of $[\eta]$ in the above temperature range has been explained by the high energy of the hydrogen bonds, which exceeds the energy of the thermal motion of the chain units; this fact indicates indirectly the occurrence of intramolecular structure formation[58,60]. Since a marked temperature variation of the degree of decomposition of hydrogen bonds is characteristic of a model low-molecular-weight analogue (isobutyric acid, i.e. hydrogenated MAA), [73] one may say that the chain structure of CCC macromolecules introduces specific features into the mechanism of the formation and decomposition of these bonds. It has been suggested[73] that the equilibrium between the free and bound COOH groups in CCC solutions is determined by the effective concentration of active groups within the macromolecular coil, and not by their overall concentration in solution, as for hydrogenated MAA. The data showing the independence of the number of hydrogen bonds within the chain of temperature in CCC solutions are consistent with the results of the study of these copolymers in the solid state; the entire set of data obtained confirm the conclusion that the energy of polymer–polymer hydrogen bonds is fairly high.

The problem of the influence of the CCC concentration in solution on the nature of hydrogen bonds formed is of interest. Infrared spectroscopic data have shown[73,74] that only hydrogen bonds within the chain are observed for the styrene–MAA (3.1 wt.% MAA) copolymer in toluene and carbond tetrachloride at CCC concentrations up to 5%; under these conditions, the proportion of free carboxy-groups is 11% and the remaining groups form dimers[74]. The low probability of intermolecular association of the macromolecules of a hydrogen-bonded copolymer of mono- and di-butyl itaconate is indicated by infrared spectroscopic and osmometric data in dilute solutions[80]. The linearity of the variation of the intrinsic viscosity with CCC concentration up to 2.5% is evidence for the absence of interchain association of styrene – MAA (2–5% MAA) copolymer macromolecules in benzene[81].

The absence of interchain association of CCC macromolecules in dilute solutions is significant in connection with the problem of the determination of the CCC molecular weight. One must take into account the range of molecular weights: it has been established[82] that the association of polystyrene molecules containing terminal carboxy-groups is observed in toluene for low-molecular-weight specimens (3×10^4); on the other hand, specimens with a higher molecular weight in dilute solutions do not form such associated species owing to the reduced probability of contacts between COOH groups belonging to different macromolecules. The situation changes with increase of the concentration of the CCC solution. On passing from a very dilute CCC solution in an inert solvent to a concentrated solution, three different concentration ranges were discovered[83]: (1) the system contains individual macromolecules and small associated species (dilute solutions); (2) an incomplete fluctuation network, made up of interchain hydrogen bonds with a finite lifetime, is in equilibrium with associated species and individual macromolecules (moderately concentrated solutions); (3) there exists a fluctuation network incorporating all the macromolecules present (concentrated solutions). The significant differences between the regions are manifested by the fact that the introduction of a proton acceptor into dilute solutions leads to a dissociation of the hydrogen bonds within the chain and to an increase of the reduced or characteristic [intrinsic] viscosity of the CCC solutions, whereas in the second and third concentration ranges a decrease of the viscosity of the CCC solution is observed after the addition of the proton acceptor[69], because the viscosity of these solutions is determined primarily by the interchain contacts and the proton acceptor disrupts those which are due to hydrogen bonds. Even gel formation is possible in the absence of a proton acceptor[84].

The study of the concentration dependence of the Newtonian viscosity of the styrene–acrylic acid (4% of acrylic acid) copolymer under the conditions of maximum (toluene) and minimum (toluene + 20% DMF) formation of hydrogen bonds made it possible to discover[69] the concentrations characterising the critical conditions for the transition from a dilute to a moderately concentrated (c'_{crit}) solution and from a moderately concentrated to a concentrated solution (c_{crit}). At the concentration c'_{crit} the formation of a three-dimensional hydrogen bond network in the CCC solution begins, while at the concentration c_{crit} its formation is completed. It has been found for the above copolymer (degree of polymerisation 2.5×10^3) that $c'_{crit} = 4.36$ and $c_{crit} = 6.9$ g dl^{-1} in toluene, whereas in toluene

containing 20% DMF, these concentrations are 2.08 and 12.9 g dl^{-1} respectively.

The data presented show that the transitional region in which the formation of the complete three-dimensional network begins and is completed throughout the bulk of the solution becomes significantly extended under conditions of the minimum formation of hydrogen bonds of the polymer–polymer type, whereas in toluene this process takes place over a fairly narrow concentration range. The maximum rupture of hydrogen bonds within the chains between carboxy-groups promotes the unravelling of the coil; as a result of this, the network of interchain bonds in the copolymer in the toluene + DMF mixture begins to be formed at lower concentrations c'_{crit} than in pure toluene owing to the greater probability of the formation of interchain contacts. The probability of the formation of such contacts increases also with increase of the molecular weight of the CCC, which promotes a decrease of both critical concentration[69]. Thus the formation of a hydrogen bond network in fact determines the conditions for the transition from one concentration range to the other.

The study of the rheological properties of solutions of MMA–MAA copolymers established that the ability to form interchain hydrogen bonds is the fundamental cause of a whole series of observed effects. Thus the fluctuation network of the interchain hydrogen bonds hinders the disruption of the structure of the CCC solution in an inert solvent and causes its antithixotropic stabilisation both under the conditions of simple shear and for complex (predominantly longitudinal) flow deformations[49,51,52,54,63,83]. When this type of three-dimensional network is created, the transition from one thermodynamic state of equilibrium to another is hindered and the relaxation time τ_0 increases significantly[63,85]. The appearance of an excess heat of activation for the viscous flow of the CCC solutions is also regarded as a result of the same structure-formation effect[62,69,83,85–88] and the increment in the heat of activation ΔU depends both on the content of carboxy-groups in the copolymer (U increases in proportion to the logarithm of the molar content of MAA units[83,87,88]) and on the presence of added proton acceptors in an inert solvent. Experimental data indicate an unambiguous correlation between the heat of activation for viscous flow and the density of effective interchain contacts due to hydrogen bonds, which makes it possible to regard U in the region of moderately concentrated CCC solutions as a measure of the density of the three-dimensional fluctuation network formed[62]. In fairly dilute solutions a sharp increase of U with concentration is observed, but the formation of a complete hydrogen bond network throughout the bulk of the concentrated solution causes an asymptotic approach of U to a constant (for a given molecular weight and a given composition of the copolymer) value, which is virtually independent of the concentration of the copolymer in the inert solvent for $c > c_{crit}$.[69,83,87,88] The higher the molecular weight of the copolymer and the higher the molar content of the MAA units in it, the lower the critical concentration after the attainment of which U becomes constant. It has been suggested[87] that the independence of U of c in this concentration range is consistent with the idea that, for a fairly large number of bond nodes (contacts), U is independent of the number of nodes for the given copolymer and depends solely on their nature[89].

As in dilute solutions, the introduction of a small amount of a proton acceptor into an inert solvent causes the rupture of the polymer–polymer hydrogen bonds in CCC and to a large extent weakens or completely eliminates the effects mentioned above, which confirms that they are due to the selective interchain interactions between groups capable of forming a hydrogen bond.

Analogous relations, due to the presence of stronger interchain contacts, have been discovered also in the study of the viscous and relaxation properties of poly(methacrylic acid) solutions in methanol, ethanol, and ethylene glycol in the concentration range 9–20%.[90] In this case the dihydric alcohol behaves as a cross-linking agent forming hydrogen bond bridges between the macrochains. As a result of this, the "relaxation viscosities" and durations of the initial period of the relaxation of strain in poly(methacrylic acid) solutions in ethylene glycol are greater by approximately three orders of magnitude than in monohydric alcohols at the same polymer concentration.

Data for the dependence of a whole series of characteristics of CCC solutions on concentration over a wide range of the latter showed that the concentration of a real CCC solution as such cannot serve as a criterion of its being dilute or concentrated, because the limits of the existence of solutions with and without strengthened interchain contact are not absolute, are mobile, and are determined primarily by the composition of the copolymer and its molecular weight as well as the ability of the solvent to compete with the polymer in the formation of hydrogen bonds. For CCC, with their ability to undergo selective interactions, only analysis of the properties of a specific system can provide an answer to the question whether the macromolecules in the given solution are isolated from one another, or whether there are contacts of a definite type between them up to the formation of a complete fluctuation network throughout the bulk of the system[88].

IV. THE INFLUENCE OF IONIC INTERACTIONS ON THE PROPERTIES OF MONOMERS IN BULK

The neutralisation of some of the carboxy-groups in CCC by metal ions of different valence leads to the enrichment of the spectrum of the possible types of selective interactions and hence to the appearance of a series of specific properties in such polymers (ionomers) in both the solid state and in solutions.

The hydrogen bond joins together only two functional groups ($n = 2$) of the macrochain, whereas electrostatic forces, which are in addition capable of acting over a long distance, can lead to the formation of very large ionic associated species ($n \geq 2$). The preferred interaction of solvent groups with one another in ionomers is also caused by their definite incompatibility with the hydrocarbon chain units. The existence of ionic accumulations (clusters and multiplets) in the bulk of the monomer has been justified theoretically[91]; the concept of cluster formation constitutes the basis of the interpretation of the majority of experimental data in recent years, obtained in the study of ionomers in the solid state. To a first approximation, one may assume that the decrease of segmental mobility in consequence of strong ionic interactions is the main cause of the increase of mechanical moduli and the decrease of the elasticity of ionomers compared with the corresponding carboxyl-containing copolymers[15,32,33,92].

The replacement of acid groups by salt groups significantly retards crystallisation up to its complete disappearance in copolymers of ethylene with acrylic acids[4,5,31,93], the influence of the neutralisation of carboxy-groups on the crystallisation kinetics being shown to the greatest extent for copolymers containing 1–7 mole % of the acid. Internal structural rearrangement due to ionic cross linking lead to an appreciable increase of T_g for ionomers (in a

particular ion concentration range) compared with CCC[7-9,11,12,14,15,25,94-101]; additional transitions are also observed in ionomers. In the discussion of problems concerning the influence of ionic cross links on the transition temperatures, the following factors must be taken into account. In contrast to covalent cross links, whose position in the specimen is rigorously fixed, ionic cross links in ionomers exhibit a definite mobility owing to the ability of cations to migrate in the bulk of the specimen. The results of a study of a mixture of an ethylene copolymer with acrylic acid and its ionomer in which the degree of neutralisation is 70%[92] showed that in mixtures of this kind regions rich in ions act as ion donors for the entire system, which becomes identical as regards its properties with an ionomeric specimen having a degree of neutralisation of 35%.

The inc rease of the segmental mobility of the chains with temperature also gives rise to greater possibilities for the redistribution of ionic cross links in the bulk of the specimen. It cannot be ruled out that, when T_g and T_y are reached, ionic associated species of one kind break down (otherwise the specimen would not have softened and would not have passed into a fluid state) and ionic accumulations of a new type are generated; the appearance of such ionic inhomogeneities is opposed by the entropy factor. Since the degree of Coulombic interaction is independent of temperature, particular types of ionic associated species will be manifested in the ionomer specimen at any temperature. Infrared spectroscopic data for ionomers of different structure suggest[102,103] the existence of a whole set of ionic associated species of different structure, whose relative content varies with temperature.

The transition temperatures in ionomers are to a large extent determined by the content of acid groups in the copolymer and by the degree of their neutralisation[97]; in certain cases ionic cross links are so strong that they do not break even on heating to approximately 400°C (ionomers with a high degree of neutralisation based on graft ethylene–maleic anhydride copolymers). It was shown in the above study that[97] the nature of the cation also affects the transition temperatures: for the same degree of neutralisation, the softening and yield temperatures (T_s and T_y) for sodium ionomers based on statistical styrene–MAA (8 : 2) copolymers are greater than T_s and T_y for copolymers neutralised by rubidium ions. Thus the transition temperatures in sodium ionomers correspond to stronger ionic cross links formed by the Na^+ cation, which has a smaller radius than the Rb^+ cation.

It has been established for poly(acrylic acid) salts[104] and $T_g = 730\ (q/r) - 67$, where q is the charge of the cation and r the average distance between the centres of the charges of the cation and anion. This type of correlation between T_g and q/r id common to ionogenic polymers and is confirms the dependence of the transition temperatures of the electrostatic interactions in ionomers. Analysis of the available data shows[11] that one cannot rule out the possibility that the observed changes in the transition temperatures are caused by the possible operation in ionomers of a completely different flow mechanism than the segmental displacement occurring in the usual hydrocarbon polymers. The unusual nature of ionic cross links causes ionomers to behave at low temperatures as cross-linked polymeric materials, while at high temperatures they can melt[15].

The presence of additional stronger contacts between the ionomer macrochains owing to ionic interactions leads to a change of the kinetics and thermodynamic parameters of the sorption of solvent vapours. Neutralised CCC specimens, cross-linked by divinylbenzene, have appreciably lower swelling coefficients than the same copolymer in an acid form[105] and the introduction of urea into the system—an agent which actively breaks hydrogen bonds—entails an increase of the degree of swelling of the specimen also in a partly neutralised form. With increase of the degree of neutralisation of carboxy-groups in the ionomer, there is an increase in the resistance of the system to the action of a solvent capable of competing with the polymer in the formation of hydrogen bonds, as shown by the decrease of the rate of attainment of sorption equilibrium, the decrease of the diffusion coefficient of the solvent, and the corresponding increase of the activation energy for this process[28,106]. On passing to a significantly neutral solvent (toluene), it was observed[28] that the amount of sorbed solvent (in a state of equilibrium) in the styrene–acrylic acid (3.9% of acrylic acid) copolymer passes through a minimum and maximum when the degree of neutralisation (α) is 5–15% and 50% respectively. The authors[28] suggest that the increase of the resistance of the structure to the action of the solvent in the region of α = 5–15% is due to the strengthening of the existing fluctuation network of hydrogen bonds owing to additional interactions of the salt group. However, in the region α = 25–50% there is an "inversion of networks": a transition from hydrogen bonds to a lattice of ionic clusters. The imperfection of the network in this transitional region leads to the weakening of the interchain interactions in the ionomer, which is reflected in the experiment by an increase of the degree of sorption of toluene. For $\alpha > 50\%$, a kind of framework of clusters made up of metal ions, which significantly stabilises the ionomer structure, is formed.

Thus comparison of certain characteristics of CCC and their ionomers shows that the effects caused by the introduction of units with carboxy-groups into the hydrocarbon polymer chain change appreciable on partial neutralisation of these groups by metal ions. The characteristics of the properties of complex polymeric formations such as ionomers are in many respects caused by the superposition of the influences of hydrogen bonds and ionic interactions, the proportions of which are determined by the degree of neutralisation.

V. THE PROPERTIES OF SOLUTIONS OF COPOLYMERS WITH IONOGENIC SALT GROUPS

Whereas the physicochemical properties of ionomers in the condensed state are being investigated fairly vigorously, the number of studies on the conformation and transformations and behaviour of ionomers in solutions is not so great. Nevertheless certain common features in the variation of the conformational parameters of isolated CCC molecules on replacement of the protons of the carboxy-groups by various metal ions have been quite clearly demonstrated. The appearance of salt groups leads to sharp changes in interactions within the chains, the intensity of which in dilute solutions is inferred mainly from the intrinsic (characteristic of reduced) viscosity. The polarity of the solvent, its capacity to induce the dissociation of salt groups, exerts the primary influence on these interactions.

It is significant that, in contrast to neutralised homopolymeric acids, ionomers can be investigated (as a function of their composition) in solvents with a wide range of dielectric constants, although an organic solvent cannot be selected for some of them. The poor solubility of ionomers is caused by the extreme diphilic properties of their

macromolecules — the combination in one chain of a non-polar (hydrocarbon) unit and units with salt groups. It is therefore impossible to select for ionomers a solvent which will have the same or at least similar thermodynamic affinities for units of both types. The presence of inter-chain bond nodes in the form of ionic multiplets and clusters imparts to ionomers a high resistance to oil and motor fuel, because the action of organic products with a low dielectric constant cannot lead to the rupture of inter-chain ionic bonds.

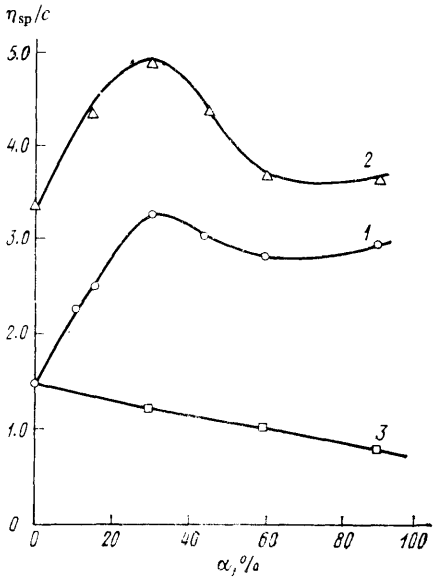


Figure 1. Dependence of the intrinsic viscosity ($c = 0.3\%$) on the degree of neutralisation of ionomers based on the styrene–methacrylic acid copolymer: *1*) Na-ionomers in DMF; *2*) Na-ionomers in DMF + 2% of water; *3*) Zn-ionomers in DMF. [75]

However, the same factors which ensure the notable physicomechanical properties of ionomers (including resistance to the action of solvents) complicate their study in solutions. In the first place the choice of solvent is made much more difficult and, what is most significant, in the study of a given ionomer it is usually impossible to use a wide range of different solvents. Another complication concerning the interpretation of data obtained in the study of the properties of ionomer solutions is due to the fact that, whereas hydrogen bonds of the polymer–polymer type can be completely destroyed by selecting a special solvent, electrostatic interactions in ionomer solutions always occur. By altering the nature of the solvent as a result of the introduction of various additives, it is possible to alter only the intensity of these interactions (both by changing the dielectric constant of the medium and by the solvation of ionic species). In solutions of ionomers a wide variety of intramolecular and intermolecular interactions (dipole–dipole, dipole–ionic, ionic, hydrogen bonds) can be manifested in principle. The real possibility of the manifestation and the intensities of particular interactions are determined by the specific nature of the ionomer and the solvent.

In a viscometric study in DMF ($\epsilon = 36$) the manifestation of polyelectrolyte swelling in the macromolecules of sodium ionomers, based on methacrylic acid copolymers, was noted[75,107–110]. The replacement of acid groups by salt groups, results in an increase of the ionogenic capacity in the region of dilute solutions. However, with increase of the concentration of the solution (up to 6%), the degree of ionisation falls appreciable[108]. The almost complete dissociation of salt groups with a univalent cation in ionomers based on the MMA–MAA copolymer (in DMF as the solvent) has been demonstrated also by electrochemical methods[111–113]. Bivalent metal ions interact with carboxylate groups of the ionomer chains so vigorously that the polyelectrolyte effect is as a rule not observed even in solvents with a fairly high polarity[75,114,115]. The study of electrolyte transfer in such systems also confirms the virtually complete absence of the dissociation of the salt groups of the macrochain, whereas the monomeric alkaline earth metal salts of methacrylic acid dissociate in DMF[111,116].

The macromolecules of ionomers based on acrylic acids containing univalent metal ions undergo a conformational transition in the course of ionisation in polar solvents[75,117]. The initial increase of intrinsic viscosity (Fig. 1) indicates a successive unravelling of the polyelectrolyte coil with increase of the number of ionogenic salt groups; the subsequent decrease of η_{sp}/c is due to the intense binding of sodium counterions and the consequent decrease of the effective number of charges on the chain. The onset of the conformational transition is determined by the content of the unsaturated acid in the copolymer. The occurrence of the conformational transition is confirmed also by potentiometric titration data[117]. Comparison of the viscometric behaviour of Na and Zn-ionomers based on the styrene–MAA (8:2) copolymer in the same solvent shows (Fig. 1) that there is no conformational transition in Zn-ionomers. This serves as yet another piece of evidence for the difference between the ionisation-dissociative processes in the methacrylate salt groups of ionomers in a polar solvent as a function of the nature of the metal.

When a highly polar solvent such as formamide ($\epsilon = 109$) is used, a sharp increase of the intrinsic viscosity of the sodium ionomer (degree of neutralisation $\alpha = 0.8$) is observed compared with the corresponding copolymer of ethyl acrylate and acrylic acid in an acid form[118]. Thus, in a medium with a fairly high dielectric constant, the macromolecules of ionomers with univalent cations exhibit the characteristic hydrodynamic and electrochemical features of polyelectrolytes.

However, the study of solutions of ionomers in weakly polar solvents is of great interest. A medium with a low dielectric constant imitates to a definite extent the environment of the ionomer macromolecule in bulk; furthermore, non-polar solvents in the majority of cases solvate ionic species very weakly. For this reason, in media of this kind the conditions for electrostatic interactions, which occur in solid ionomers and lead to the formation of ionic associated species, are established to the maximum extent. This ensures a direct relation between the results of a study of ionomers in weakly polar solutions and the results of their study in the condensed state. The transition to significantly non-polar solvents implies primarily an impairment of the solubility of the ionomer salt units and an intensification of electrostatic interactions. Such solvents exhibit a weak dissociating capacity; for $\epsilon < 10$ to 15, the dissociation of the solute hardly occurs and free ions are absent from the solution. Media with a low dielectric constant exhibit a characteristic tendency towards the formation of complex ionic species, such as

ion pairs, ion triplets, quadrupoles, and other higher-order aggregates[119]. The less polar the solvent the greater probability of the existence in the latter of contact ion pairs. All these factors, acting together, lead to a number of characteristics of the hydrodynamic properties and conformations of ionomer macromolecules in such solvents.

Judging from the experimental data[66,67,70,72,75,81,115,120-124] obtained using non-polar solvents or under the conditions of suppressed dissociation, in all cases a high degree of neutralisation of the carboxy-groups in CCC via metal ions is accompanied by the contraction of the macromolecular coil, as shown by the decrease of the intrinsic viscosity (or the specific or reduced viscosity at a low concentration) and by the increase of the diffusion coefficients of the ionomers compared with the corresponding copolymers in an acid form. The polyelectrolyte swelling in ionomers is not observed in this case. The contraction of the coil increases with increasing number of ionogenic salt groups in the macrochain (Figs. 2–4). The Huggins constant varies in opposition to $[\eta]$ with increase of the degree of neutralisation of carboxy-groups[66]. Although the conformation of the ionomer macromolecules in dilute solution is determined by the competing effects of forces of different kinds, experiment showed that forces drawing together the macromolecular coil predominate in this instance. The problem of their nature arises.

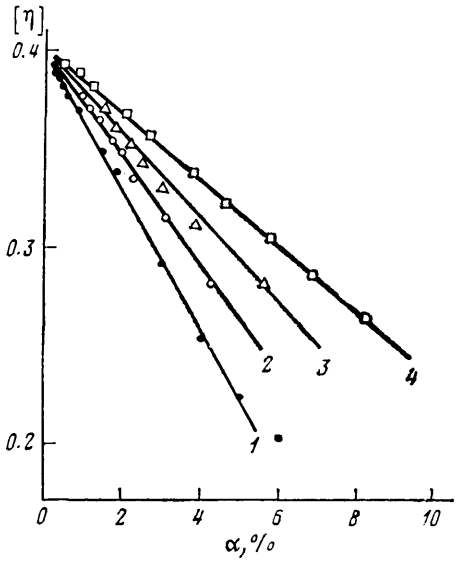


Figure 2. Dependence of the intrinsic viscosity in 1-octanol on the degree of neutralisation of Na-ionomers (line *1*), K-ionomers (line *2*), Cs-ionomers (line *3*), and Ca-ionomers (line *4*) based on the alternating maleic acid–hexadecyl vinyl ether copolymer[122].

The decrease in the size of the coil as a result of its contraction is associated primarily with the impairment of the thermodynamic quality of the solvent (non-polar solvents do not dissolve acrylate salts). This is also indicated by the increase of the Huggins constant on passing from the copolymer in an acid form to the ionomer. The thermodynamic factor promoting the aggregation of the ionomer salt groups within the chain is strengthened by electrostatic interaction forces between the ion pairs formed (here it is extremely significant that the Coulombic forces act over a long distance). The viscometric characteristics of the ionomers containing various metal ions constitute the most convincing evidence for the primary influence of ionic interactions on the conformational characteristics of their macromolecules. If the decrease of $[\eta]$ were caused solely by the impairment of the thermodynamic quality of the solvent, a clear cut dependence of $[\eta]$ on the nature of the cation introduced into the polymer would not have occurred (see Figs. 4–5 and literature data[81,107,110,112,115,121]). An increase of the radius of the cation leads to a weakening of the ionic interactions favouring the contraction of the coil. Accordingly, ionomers with a larger radius of the cation, introduced for the same charge of the latter, have a higher intrinsic viscosity.

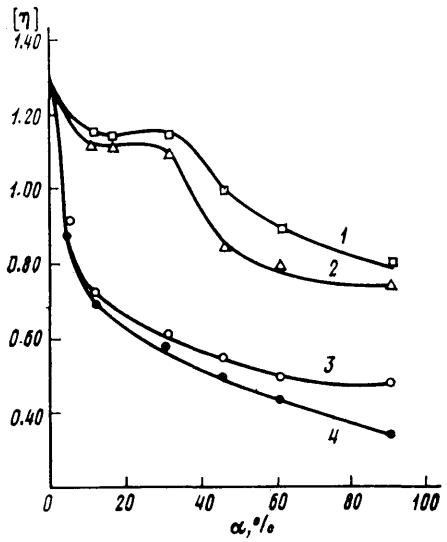


Figure 3. Dependence of the intrinsic viscosity in DMF + 0.05 M NaI on the degree of neutralisation of the Rb-ionomers (curve *1*), Na-ionomers (curve *2*), Ca-ionomers (curve *3*), and Zn-ionomers (curve *4*) based on the styrene–methacrylic acid copolymer[75].

The joint action of the thermodynamic factor and electrostatic interaction forces leads to the formation and stabilisation of ionic associated species of different degree of complexity, which can be regarded as stable bond nodes within the chains of ionomers in dilute solutions (the absence of interchain ionic interactions under these conditions has been confirmed by the equality of the molecular weights of the CCC before and after neutralisation[75,81,123]). An ionic quadrupole is formed in the simplest case under these conditions[81].

$$2\left\{\text{—COO}^{-}+\text{M}\right. \rightleftarrows \begin{matrix}\left\{\text{—COO}^{-}+\text{M}\right. \\ \left.\text{M}^{+}\text{-OOC—}\right\}\end{matrix}.$$

Such "cross linking" within the chain as a result of the interaction of two ion pairs does not differ in principle, as regards its effect on the size of the coil, from cross linking due to the formation of a dimeric hydrogen bond between carboxy-groups. However, experimental data show that the interaction between the salt groups of ionomers in non-polar solvents has a more effective influence on the contraction of the isolated coil than hydrogen bonds[70,72,81]. In the case of hydrogen bonds the number of cross-linked units is two. It has been found by infrared spectroscopy and viscometry for the sodium ionomer based on the styrene–acrylic acid (1.74% of acrylic acid) copolymer that the average number of ion pairs in ionic associated species is four[70,72].

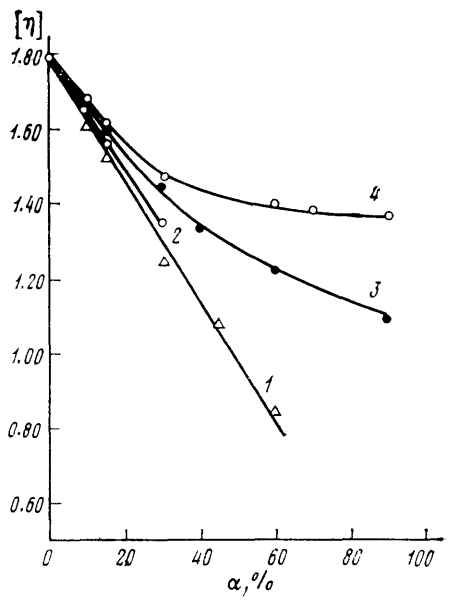


Figure 4. Dependence of the intrinsic viscosity in tetrahydrofuran on the degree of neutralisation of Na-ionomers (curve *1*), Rb-ionomers (curve *2*), Zn-ionomers (curve *3*), and Ca-ionomers (curve *4*) based on the styrene–methacrylic acid copolymer[75].

The set of data obtained for dilute solutions of sodium ionomers based on statistical styrene–MAA copolymers of different compositions suggests that the characteristics of the hydrodynamic behaviour and conformations of the ionomer macromolecules are determined by the formation of fairly large ionic associated species, which can behave as a disperse intramolecular microphase[124,125]. This type of microprecipitation phenomenon with all its consequence is characteristic only of block copolymers in selective solvents[126–130]. The observed specific feature of ionomers with a statistical distribution of units in the chain makes it possible to regard them as pseudo-block copolymers in solution. The intramolecular aggregation of ion pairs is not accompanied by the dissociation of interatomic bonds and a change in the sequence of units, i.e. the primary structure of the statistical copolymer chain is maintained. The secondary structure arising under these conditions imparts to the ionomer macromolecules a conformation more complex than that of the statistical coil.

One must bear in mind that the increased concentration of units with salt groups in the separate regions within the ionomer macrochain is a factor promoting an increase of the local electrostatic potential, enhanced binding of the metal cations, and the formation of ionic associated species with a size such that they begin to behave as a heterogeneous microphase. As an example of the influence of the mode of distribution of salt groups in the chain on the strength of the binding of counterions, one may refer to a study[131] where it has been shown that, for the same monomer ratio, aqueous solutions of sodium salts of the methyl acrylate–acrylic acid copolymer with salt units arranged in groups along the chain have a lower viscosity than solutions of the copolymer with a uniform (statistical) distribution of sodium acrylate units. Thus, even in aqueous solution, the arrangement of salt units in groups promotes an enhanced binding of counterions and the contraction of the coil; in a non-polar medium all these processes are additionally enhanced by the incompatibility of the salt groups and the solvent.

In this respect the hydrogen bonds in CCC are manifested in the opposite way[57,61,64]. The considerable concentration of unsaturated acid (or its salt) units in groups along the macrochain leads to a weakening of the influence of the hydrogen bonds and an enhancement of the influence of ionic interactions on the size and structure of the macrocoil in an inert non-polar solvent. Hydrogen and ionic bonds may prove to be comparable as regards the strength of their influence on the internal structure of the coil when the copolymer chain contains a small amount of statistically distributed units of the unsaturated acid or its salt; in this case both interactions are mainly pair interactions (the formation of large ionic associated species is unlikely) and the intrinsic viscosities of solutions of such copolymers in the acid and ionomeric forms are virtually the same[66,67,69].

It can be assumed that the selective interactions of the salt groups with one another, the formation of ionic associated species, and their segregation as a microphase occur in ionomer solutions for the same reasons as in the bulk of the ionomer (the incompatibility of the salt groups with the hydrocarbon part of the chain and electrostatic interactions). However, in solutions the formation of ionic associated species is also promoted by the thermodynamic incompatibility of the salt units with the weakly polar solvents usually employed for ionomers. The presence of a microphase in the form of ionic associated species determines the specific features of the behaviour of ionomers not only in the condensed state but also in dilute solutions.

The validity of the idea of the dominant role of ionic interactions within the chain and intense intramolecular processes as the most characteristic feature of isolated ionomer macromolecules in solution is confirmed by experimental data. All the methods for altering the strength of electrostatic interactions lead to an appreciable alteration of the conformation of the coil, which is usually observed by measuring the intrinsic viscosity. The strength of ionic interaction within the chain may be regulated by changing the charge density on the chain (i.e. the degree of neutralisation), by altering the radius and charge of the cation introduced into the ionomer and the dielectric constant of the medium (solvent), or by introducing into the solution small amounts of substances capable of active solvation of the cations. The data quoted

above reflect the influence of the majority of these factors on the strength of ionic interactions.

The interesting possibility of a specific influence on the order of ionomer macromolecules within the chain and on their solubility can be realised by taking into account the nature of solvation phenomena. The fact that the solvent exerts a significant influence on the strength of ionic interactions within the chain in ionomers precisely by virtue of its solvating activity has been confirmed by the following experimental data. In a salt solution in DMF ($\epsilon = 37.6$) ionomers based on the styrene–MAA copolymer containing univalent metal ions have appreciably lower values of $[\eta]$ than ionomers based on the same copolymer but containing bivalent metal cations[75] (Fig. 3). Bivalent metal cations are bound by the polymeric ion more effectively than univalent cations. However in tetrahydrofuran (THF) ($\epsilon = 7.4$) the opposite behaviour has been observed for the same specimens[75] (Fig. 4): ionomers with univalent cations have a lower intrinsic viscosity. This is apparently due to the formation in this non-polar solvent of contact ion pairs for ionomers with univalent metals and solvate-separated ion pairs for the macromolecules of ionomers with bivalent metals. A similar dependence of $[\eta]$ on the charge of the counterion has been observed (Fig. 2) for neutralised specimens of the alternating maleic acid–hexadecyl vinyl ether copolymer in 1-octanol ($\epsilon = 10.3$); the calcium ionomer dissolves in this solvent even for $\alpha = 40\%$, while the sodium ionomer dissolves only up to $\alpha = 10\%$.[122] However, it must be emphasised that for ionomers the nature of the dependence of $[\eta]$ on the valence of the metal introduced into them is determined, apart from the nature of the solvent, also by the characteristics of the structure of the macro-chain. Thus in a salt solution in DMF ionomers based on the alternating maleic acid–hex-1-ene copolymer have a high value of $[\eta]$ when the chain contains bivalent metal cations[132], in contrast to ionomers based on the statistical methacrylic acid polymer[75].

When a non-polar solvent is treated with small amounts (several per cent) of other solvents capable of solvating metal cations more actively, an appreciable increase of the size of the macrocoil, i.e. of $[\eta]$ of the ionomer, is observed[66,67,70,72,75], although both the thermodynamic quality of the solvent and its polarity are hardly affected thereby on the macroscopic scale. The unravelling of the coil under these conditions is due to the weakening of the ionic interactions and the possible breakdown of large ionic associated species, because a weaker electrostatic field is generated around the solvated cation and the energy of the Coulombic interaction diminishes under these conditions. When solvents appreciably more polar than the main solvent are added, account must be taken of the significant increase of the local dielectric constant of the medium owing to the selective solvation of ion pairs by the more polar component of the solvent (this effect is manifested to a particularly large extent when water is added to an organic solvent, which is accompanied, as can be seen from Fig. 1, by the enhancement of the polyelectrolyte unravelling of the ionomer coil).

However, the influence of solvation processes on the intensity of ionic interactions can be followed in the "purest" form[75] (Fig. 5) in relation to sodium ionomers using pyridine (5 vol.%) as an additive to THF. In this case both components of the solvent have similar polarities and both pure THF and THF with additives contain no "cross links" within the chains due to hydrogen bonds. Fig. 5 shows that the addition of pyridine ($\epsilon = 12.3$) to THF ($\epsilon = 7.4$) increases the intrinsic viscosity of the ionomeric specimens, because pyridine solvates sodium cations more actively and diminished thereby the intensity of the electrostatic interactions and the contraction of the coil. The weakening of ionic interactions within the chain in sodium ionomers in the presence of pyridine is manifested most clearly for $\alpha > 30\%$, i.e. in the region of the concentration of salt groups, for which the probability of the formation of large associated species increases. It is instructive that the ionomer with $\alpha = 90\%$ does not dissolve in THF, whereas in the presence of pyridine it does so. A similar improvement of the stability of ionomers is achieved by adding acetic acid[75] and methanol[121] to THF. Ionomers based on ethylene dissolve only in mixed solvents consisting of an organic solvent having a solubility parameter $\delta = 8$–9 and acetic acid[22].

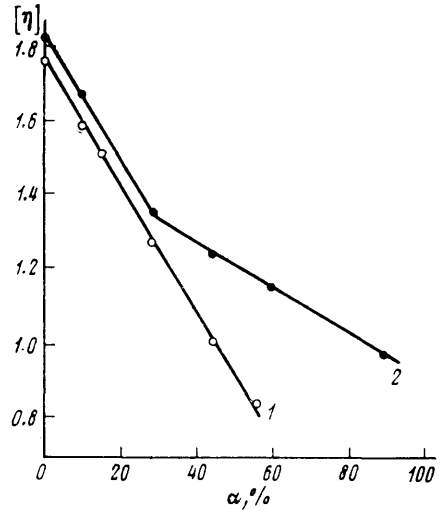


Figure 5. Dependence of the intrinsic viscosity on the degree of neutralisation of Na-ionomers based on the styrene-methacrylic acid copolymer; solvent: *1*) tetrahydrofuran; *2*) tetrahydrofuran + 5% of pyridine[75].

The choice of additives improving the solubility of ionomers is complicated by the fact that the main characteristics of the solvation of metal cations in non-aqueous media have still not been fully discovered, and comparative estimates of the solvating powers of solvents are not always correlated with their dielectric constants and dipole moments, because covalent σ and π interactions between the cation and the solvent molecule sometimes predominate over electrostatic (ion–dipole) interactions[133]. Significant changes in the solubility and hydrodynamic properties of ionomers can be expected when additives capable of forming complexes of the metal cations in the ionomeric are introduced into the inert solvent, particularly cations with *d* electron shells, whose high capacity of solvation is determined mainly by the donor–acceptor interactions with the solvent. This question still requires experimental tests.

In conformity with the concept of the dominant influence of ionic (electrostatic) interactions on the conformational characteristics of ionomer macromolecules, the size of the coil (for ionomers with univalent metal cations) is

independent of temperature in the range between -40° and +70°C, judging from viscometric data[107,120]. Furthermore, on passing to ionomers with bivalent metal cations, it has been noted[134] that the specific viscosity of their solutions decreases appreciably with increasing temperature. However, this finding not only does not conflict with the main concept but actually serves as one of its confirmations. The point is that an increase of temperature promotes the desolvation of cations, which is particularly pronounced for a bivalent metal cation, and this leads to an enhancement of their binding by the macrochain[135,136]. Under these conditions, the coil undergoes additional contraction, which is observed experimentally as a decrease of the viscosity of the ionomer solution[134]. In the discussion of the problem of the temperature dependence of the conformational parameters of the ionomer chain one must take into account the fact that the degree of desolvation is determined not only by the charge of the cation, but also by the nature of the solvent and the detailed mechanism of their interaction.

As shown above, the hydrodynamic properties of ionomers vary with the chemical nature of the cation introduced. The characteristics observed under these conditions are related in a definite manner to solvation phenomena and make it possible to determine the type of interaction between the counterion and the macrochain.

A definite view has now been formulated concerning the principal types of counterions in polyelectrolyte solutions. This problem has been dealt with in detail in reviews[137-145]. It is possible to distinguish three types of counterions: "free", "specifically bound", and "diffuse" or "atmospheric". Free counterions are not directly influenced by the electrostatic potential of the polymeric ion. The number of such counterions is fairly small even in aqueous polyelectrolyte solutions; their number in solutions with a reduced dielectric constant is even smaller, particularly in the case of bivalent counterions, as can be seen from the data presented at the beginning of this Section concerning the hydrodynamic and electrochemical properties of ionomer solutions.

The idea of the specific binding of counterions was first put forward in the study of aqueous solutions of polyacrylic acid salts[146,147]. Such counterions are associated with fixed ionic groups of the polymeric ion. As a result of this kind of binding in solution (even aqueous solutions), ion pairs and other more complex ionic formations and complex and chelate compounds are produced. The most important feature of the specific binding consists in the alteration of the solvent structure in the immediate vicinity of the polymeric ion and the counterion as a result of the desolvation or at least the reorganisation of the medium around the ion.

Diffuse or atmospheric counterions are subject to the influence of the electrostatic potential of polymeric ions, but they are not associated with the latter quite as strongly as specifically bound counterions. These ions form an ionic "atmosphere" around the polymeric ion and are retained in the vicinity of the latter exclusively by virtue of Coulombic interactions. Atmospheric counterions retain their solvation shells. The occurrence of specific binding does not eliminate the ionic atmosphere; the latter always exists to some extent around the polymeric ion.

The reversibility of the normal sequence of the binding of alkali metal ions by polycarboxylic acids in aqueous solutions can be regarded as direct evidence for occurrence of specific binding[148-157]. The normal binding sequence (from lithium to caesium) obeys the electrostatic interaction law, according to which the solvated ion with the minimum radius (Cs^+) is bound more strongly than the solvated ion with the maximum radius (Li^+). The opposite variation, observed for polycarboxylic acids, indicates the desolvation of counterions and hence their specific binding, which entails an increase of the viscosity of aqueous solutions of polycarboxylic acid salts in the sequence Li → Cs.

Water-soluble CCC salt exhibit a similar variation of the viscosities of the solutions as a function of the radius of the added cation: the intrinsic viscosity of such CCC salt solutions increases in the sequence Li < Na < K < Rb.[158,159]

As already mentioned above, the same type of variation of the viscosity for dilute solutions of ionomers is observed also when organic solvents are used[75,110,121,122]. Presumably the observed feature of carboxy-groups, which is manifested in the specific binding of the counterions and the formation of ion pairs in the macrochain of polycarboxylic acid salts even in an aqueous medium, should become still more pronounced for neutralised CCC in organic solvents with $\epsilon < 81$.

On passing from dilute solutions of ionomers to more concentrated solutions, there is a possibility of the formation of macromolecular associated species via interchain ionic cross links. Indeed ionomers (particularly ionomers with a bivalent metal) based on the styrene–MAA copolymer exhibit a sharp non-linear increase of the intrinsic viscosity in benzene ($\epsilon = 2.28$) with increase of the concentration above 1%, which is due to interchain association, whereas CCC itself (with MAA contents of 2 and 5%) in an acid form shows no deviations up to a concentration of 2.5%.[81] However, in dioxan ($\epsilon = 2.21$) the same monomers show no deviations from linearity up to a concentration of 2.25%. It is suggested that the relatively weak interaction between the ion pairs in this solvent can be a consequence of the solvation of the cations by dioxan. This example shows that, when solvents are compared from the standpoint of their influence on the intensity of electrostatic interactions within the chain and between different chains of ionomers, it is insufficient to take into account only the dielectric constants; one must also consider their solvating power.

In this connection one must emphasise that the selection of the solvent is particularly important in the determination of the molecular weights of ionomers. It has been found that the molecular weights of CCC and their sodium and barium ionomers with the same degree of polymerisation prove to be the same, when they are determined by light scattering in dioxan, whereas in benzene (working concentrations not in excess of 1%) the formation of interchain associated species in barium ionomers leads to an appreciable increase of the measured molecular weights[81].

The occurrence of interchain ionic interactions with increasing concentration causes such ionomer solutions (in the absence of dissociation in the given solvent) to have a higher viscosity than solutions with the corresponding copolymers in the acid form, wheras in dilute solutions ($c < 1\%$) the opposite relation is observed[75,81,121]. Similarly an increase in the degree of neutralisation (α) of carboxy-groups is accompanied by a decrease of $[\eta]$ and the viscosity of solutions of ionomers with a concentration of several per cent increases with increasing α.[75,121]

Whereas intramolecular and intermolecular association of the ionomer molecules in the presence of univalent cations takes place as a result of the ion pair interaction,

bivalent metal cations can give rise to ionic triplets of the type

$$\}\text{—COO}^-M^{2+}\ ^-\text{OOC—}\{,$$

which are much more stable than a quadrupole made up of two ion pairs, The interchain association processes of macromolecules with salt groups are therefore most instructive for solutions of ionomers containing bivalent metal cations[75,81,114,134,160]. The nature of the bivalent metal also plays an important role under these conditions: judging from measurements of the dynamic double refraction, the calcium ionomers based on the styrene–MAA (8 : 2) copolymer form in TMF rod-like aggregates containing several thousand macromolecules, while zinc ionomers give rise to molecularly disperse solutions under these conditions[115].

The interchain interactions in solutions of ionomers containing univalent and bivalent metal cations lead to structure formation and gel formation[69,114,115,120,134,160,161], the nature of the structures produced being determined (other conditions being equal) by the polymer concentration and, depending on this factor, there is a transition from the gel state to a true solution on high dilution, i.e. reversible gels are formed. The occurrence of such a transition, which is impossible in polymeric gel systems with covalent cross links, is a characteristic feature of polymers with ionogenic groups where interchain ionic cross links have a finite lifetime and exhibit a definite mobility, i.e. they can break down and reform. Similar reversible gels are produced by poly(methacrylic acid)[162] and its salts[163] in water.

The nodes of the network structure of ionomer gels in organic solvents with a low polarity consist of concentrations of salt groups (ionic associated species, ionic swarms), which leads to microlayer formation in the system[120]. The energetic non-equivalence of the nodes of the network structure of an ionomer gel has been established; this is due to the heterogeneity of the ionic associated species produced, the energy of which is between 2 and 11 kcal mole^{-1}.[120] Since the structural order in the gel state is to a large extent predetermined by the conformational characteristics of isolated macromolecules, presumably the conclusion that ionic associated species of different composition are formed and undergo microprecipitation applies equally to ionomer macromolecules in dilute solutions.

The mobility of ionic bonds in gels increases with temperature: the gel of a strontium ionomer, which is fully elastic at 20°C and is based on the MMA–MAA copolymer, passes to the viscoelastic state with increase of temperature in cyclohexanone (ϵ = 18) and at 100°C the specimen (α = 10%) acquires viscofluid properties[161]. Similar transitions have also been observed for gels of sodium monomers based on the same copolymer[120]. The transition of these systems to the viscofluid state is displaced towards higher temperatures with increasing degree of neutralisation of carboxy-groups; there is a corresponding increase also of the range of viscoelasticity and the maximum deformation in the viscoelastic state diminishes under these conditions[120,161]. In this case one may speak of a close analogy between the behaviour of ionomers in bulk and their gels under the influence of temperature, which is probably due to similar processes involving the decomposition and reorganisation of ionic associated species.

Continuing the consecutive comparison of ionic interactions and hydrogen bonds in terms of the strength of their influence on the properties of CCC and ionomers, we may note that the greatest strength of ionic bonds, compared with hydrogen bonds, is manifested most clearly in the range of concentrated solutions of the corresponding copolymers. The entire set of experimental data obtained confirm this. The results of a study[69] of the copolymer of styrene with 4 mole % of acrylic acid and its sodium ionomer (α = 25%) are very instructive in this respect. Although the intrinsic viscosities of the CCC and its ionomer in toluene are virtually the same, the transition to concentrated solutions made it possible to discover the following differences between these types of copolymers: (1) the critical concentration for the formation of a complete three-dimensional network of strengthened interchain contacts diminishes almost by a factor of two on passing from the CCC to its ionomer; (2) a high heat of activation for viscous flow has been observed in ionomer solutions; (3) in contrast to its neutralised specimen, the copolymer in the acid form does not form gels in toluene.

With increase of the ionomer concentration; even for a low content of salt groups in the macrochain, there is apparently an increase of the probability of the formation of large ionic associated species at the intermolecular level, and in such solutions there is a corresponding onset of segregation phenomena, i.e. a microphase appears. In contrast to this, in a dilute solution of an ionomer with a low content of salt groups (of the order of 1%) in the macrochain, mainly ionic quadrupoles are formed, which do not differ from the dimeric hydrogen bonds in CCC as regards their influence on the conformational characteristics of the coil.

* * *

Analysis of the results of the study of ionomers shows that the formation of ionic associated species (multiplets and clusters) is the key factor which determines the specific features of the properties of these complex polymeric structures in bulk and in solution. The results obtained suggest a particular sensitivity of the conformational parameters of ionomer macromolecules and of the internal structure of their coils to any types of influence on the intensity of ionic (electrostatic) interactions, because the latter predominate as regards the strength of their influence on the above characteristics of ionomers. However, one cannot fail to take into account also the strong selective interactions between the carboxy-groups of the copolymers. The understanding of the mechanism of the primary ordering processes within the chain (with allowance for the formation of ionic and hydrogen bonds) can lead to the discovery of methods for the specific regulation of these processes, which in many respects determine the structure and properties of the ionomeric specimen in the condensed state.

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Nuclear Magnetic Resonance Study of Polymer-Low-molecular-weight Substance Systems

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The principles of the pulsed nuclear magnetic resonance method are briefly examined. A relation is demonstrated between the measured characteristics and the parameters describing molecular motion. The characteristic features of the derivation of information about molecules in the study of complex polymers-low-molecular-weight substance systems are considered. The principal results of investigations by the NMR method of solutions of polymers, plasticised polymers, polymer gels, and compositions consisting of low-molecular-weight substances adsorbed on polymers are presented. New possibilities in the application of the NMR method are indicated.
The bibliography includes 122 references.

CONTENTS

I. Introduction 404
II. Principles of the pulsed NMR method 404
III. Polymer solutions 406
IV. Plasticised polymers 410
V. The gel state of polymers 412
VI. Low-molecular-weight substances adsorbed on polymers 414

I. INTRODUCTION

Polymer (P)-low-molecular-weight substance (LMS) systems are widely distributed in nature and technology. They include solutions of polymers, plasticised polymers, gels, and compositions consisting of small molecules adsorbed on a solid polymer. Various physical methods, one of which is NMR, are used to study such polymer systems. In many instances this method has unique possibilities. Thus it makes it possible to investigate the characteristics of the structure of complex polymeric compositions, the state of LMS molecules, the quality of the solvent, and the nature of molecular motion and helps to estimate the degree of completion of the incorporation of the LMS in the polymer, etc. However, frequently the possibilities of this method in the study of P-LMS systems are not fully appreciated and in many detailed monographs, devoted, for example, to the gel state of polymers[1] and plasticised poly(vinyl chloride) (PVC),[2] due importance is not attached to the results obtained by NMR.

The aim of the present review is (1) to describe the principal information about the pulsed NMR techniques, frequently used to investigate such compositions, (2) to examine the characteristic features of the derivation of information about molecules, (3) to describe the main results of studies on P-LMS systems, and (4) to indicate new possibilities in the application of NMR in the study of such compositions. It includes studies carried out in recent years (up to 1976) in which conclusions concerning the characteristics of the test systems have been reached from the molecular standpoint.

II. PRINCIPLES OF THE PULSED NMR METHOD

Three ways of observing NMR are used in the study of the structures and properties of matter: (1) high-resolution NMR; (2) broad-line NMR; (3) pulsed NMR. The general physical principles of the method have been described in detail in a number of monographs (for example, by Abragam[3] and Slonim and Lyubimov[4]) and will not be considered here. The characteristic features of the first method, which is one of the branches of microwave spectroscopy and makes it possible to investigate molecular structure including that of polymers, have been carefully dealt with[5,6]. The same may be said about broad-line NMR.[4,7] The most promising technique for the investigation of systems considered in this review is the pulsed NMR, the principles of which we shall describe briefly.

In order to observe the signal, the specimen is placed in a constant magnetic field H_0, at right angles to which a variable pulsed magnetic field H_1 is applied. It is generated by a pulsing microwave transmitter with a frequency $\omega_0 = \gamma H_0$, where γ is the gyromagnetic ratio of the resonating nuclei. The microwave pulse rotates the magnetisation vector $\mathbf{M}$ of the specimen by a definite angle, the magnitude of which depends on the duration of the pulse. Pulses rotating $\mathbf{M}$ by 90° ($\pi/2$ pulse) or 180° (π pulse) are usually employed. If a system of nuclei (usually protons) was at equilibrium before the application of the pulse, then $\mathbf{M}_0 \| \mathbf{H}_0$, where $\mathbf{M}_0$ is the equilibrium magnetisation of the system. After a time t has elapsed from the application of the pulse, for example, a $\pi/2$ pulse, the magnetisation vector has two components: a perpendicular component $M_\perp(t)$ and a parallel component $M_\parallel(t)$ in relation to the direction of $\mathbf{H}_0$. The nuclear relaxation process then consists in the approach of the value of $M_\perp(t)$ and of $M_\parallel(t)$ to M_0. The intensity of the signal obtained in pulsed NMR experiments as a function of the sequence and duration of the pulses is proportional to either $M_\parallel(t)$ or to $M_\perp(t)$.[8] The signal proportional to $M_\perp(t)$ is called the decrease of free induction (DFI), which is the Fourier transform of the absorption line obtained by stationary NMR methods.

Bloch suggested and it has been confirmed experimentally that

$$M_\parallel(t) = M_0[1 - \exp(-t/T_1)], \quad (1a)$$

$$M_\perp(t) = M_0 \exp(-t/T_2), \quad (1b)$$

where T_1 and T_2 are the longitudinal (spin–lattice) and transverse (spin–spin) nuclear relaxation times, which constitute additional useful information provided by the pulsed NMR method. If the NMR absorption line form is Lorentzian, then $M_\perp(t)$ is described by Eqn.(1*b*) and the line width δ is inversely proportional to T_2.

However, Eqns. (1*a*) and (1*b*) proved to be rigorously valid only for molecules containing a pair of nuclei and involved in rapid isotropic rotation. In other cases they may not hold. Thus the decreases of the values of $M_\parallel(t)$ and $M_\perp(t)$ for a three-spin anisotropically rotating system[9], four-spin systems[10], a number of polymer melts[11,12], and certain polymers in the viscoelastic state[13,14] are non-exponential, which makes it necessary to introduce effective relaxation times[11]. The spin–lattice relaxation times $T_{1\rho}$, expressed in a rotating coordinate system, are used nowadays in the study of polymer systems[8]. Studies on ^{13}C nuclear relaxation using specimens with the natural abundance of ^{13}C, have begun to develop very vigorously. The complete decoupling of the spin–spin interaction with protons, the increase of the sensitivity of pulse spectrometers, and the possibility of observing the relaxation in individual molecular fragments (CH_3–, $-CH_2-$, etc.) give rise to unique prospects for the investigation of complex polymer systems[15].

Another important characteristic of the systems, obtained with the aid of the pulsed NMR technique, is the self-diffusion coefficient D_S.[8] It is noteworthy that the method employed to measure D_S makes it possible to measure separately the translational mobility of the polymer and LMS molecules in the absence of a concentration gradient of the components.

1. Relation Between NMR Parameters and the Characteristics of Molecular Motion

The transverse and longitudinal nuclear magnetic relaxation times are magnetic parameters of the test systems and are not of independent interest in the study of polymers. However, if nuclear relaxation in polymer systems occurs as a result of the modulation of the nuclear dipole–dipole interaction of molecular motion (which occurs for the majority of polymers[4] except for polymers with conjugated bonds[16]), then it is possible to establish a relation between T_1 and T_2, on the one hand, and the characteristics of the molecular motion, on the other.

The intensity of molecular motion is characterised by the kinetic energy of the molecules E. Thus it follows from the kinetic theory that, for non-interacting molecules with a moment of inertia I', rotating about their axis with an angular velocity ω,

$$E = \frac{I'\omega^2}{2} = \frac{kT}{2}. \qquad (2)$$

If a correlation time τ_C, defined as the period of rotation of the molecule by an angle equal to one radian, widely used in NMR, is introduced in the description of molecular motion[17], then it follows from Eqn. (2) that $\tau_C^2 \propto I'/T$. Hence it is seen that, at a constant temperature, τ_C depends on the moment of inertia of the kinetic unit involved in the motion. We can therefore expect, for example, that in polymer solutions τ_C for the rotation of a segment must be greater than τ_C for the solvent molecules. If the magnetic relaxation times are related to τ_C, then there is a possibility of measuring the rate of relaxation of macromolecules and LMS molecules separately, which is in fact done in many instances.

The form of the dependence of T_1 and T_2 on τ_C is determined by the type of molecular motion of the kinetic unit and its structure. Thus we have for the isotropic rotation of molecules containing two nuclei[3]

$$T_1^{-1} = \frac{2}{5}\frac{\gamma^4\hbar^2}{r^6} I(I+1)\left(\frac{\tau_c}{1+(\omega_0\tau_c)^2} + \frac{4\tau_c}{1+(2\omega_0\tau_c)^2}\right), \qquad (3a)$$

$$T_1^{-1} = \frac{\gamma^4\hbar^2}{r^6} I(I+1)\left(\frac{3}{5}\tau_c + \frac{\tau_c}{1+(\omega_0\tau_c)^2} + \frac{2}{5}\cdot\frac{\tau_c}{1+(2\omega_0\tau_c)^2}\right), \qquad (3b)$$

where I is the nuclear spin, h the Planck constant, and r the distance between the nuclei. Analogous relations can be formulated also for the rate of relaxation determined by the translation motion of two-spin molecules[18]. If the molecular motion is described by a spectrum of correlation times, then Eqns. (3) become somewhat more complex. Expressions for T_1 and T_2, modified taking into account the τ_C spectrum, have been published by Connor[19] and Grigor'ev and Maklakov[20] respectively. It is noteworthy that equations of type (3) for relaxation occurring as a result of the segmental motion of macromolecules have been obtained only for very dilute solutions[21,22], although such equations are used frequently in the interpretation of experimental T_1 and T_2 results for block polymers or their concentrated solutions: this leads to incorrect results in many instances[23].

If the relaxation takes place via several mechanisms, then the overall relaxation time, for example, the transverse relaxation time, is of the form

$$T_2^{-1} = \sum_i T_{2i}^{-1}, \qquad (4)$$

where T_{2i} is the relaxation time corresponding to the ith mechanism.

2. Characteristics of Nuclear Relaxation in Multiphase Systems

The above discussion refers to single-phase systems, which are characterised by unique values of T_1 and T_2. It is readily seen that the polymer–low-molecular-weight substance systems are "multiphase" from the standpoint of NMR.[24] The term "phase" in NMR is usually understood as a set of magnetic nuclei characterised by a single relaxation time. The parameters of the ith phase are the relaxation times T_{1i} and T_{2i}, the population p_i, i.e. the fraction of nuclei referring to this phase, and the residence time τ_i of the nuclei in the given phase. If the nuclei pass from one phase to another, then one speaks of the occurrence of exchange in the system; the probability of the transition from the ith phase is then equal to τ_i^{-1}.

The decreases of the transverse and longitudinal magnetisations, which carry useful information about specimens consisting of n phases, can be formulated analytically[25] as follows:

(1) For "rapid" exchange, when $\tau_i \ll T_{1i}$ or T_{2i}:

$$M_\perp(t) = \exp(-t/T_{2m}), \qquad (5a)$$

where $T_{2m}^{-1} = \sum_{i=1}^{n} p_i T_{2i}^{-1}$, i.e. the transverse magnetisation of the specimen is described by a single exponential function with an average time T_{2m}.

(2) For "slow" exchange, when $\tau_i \gg T_{1i}$ or T_{2i}:

$$M_\perp(t) \sim \sum_{i=1}^{n} p_i \exp(-t/T_{2i}), \qquad (5b)$$

i.e. the decrease of magnetisation is described by the sum of the exponential functions and times characteristic of each phase. If the $M_\perp(t)$ curve is appropriately resolved[25], it is possible to obtain the values of p_i and T_{2i} for each phase.

(3) For "intermediate" exchange, when $\tau_i \simeq T_i$ or T_{2i}, calculation is possible only in the case of two-phase systems ($i = 1$ or 2):

$$M_\perp(t) \cong \sum_{i=1}^{2} p'_i \exp(-t/T'_{2i}). \qquad (5c)$$

The measured quantities p'_i and T'_{2i} in Eqn. (5*c*) differ from the true parameters p_i, T_1, and T_2 characterising the phase. For example:

$$T'_{2i} = f(T_{2i}, p_j, \tau_j), \qquad (5)$$

where $j = 1$ or 2 and the function f has been published by Zimmerman and Britten[25] and in Chernyshev's review[26] Eqns. (5) are valid if the resonance frequencies ω_0 of the nuclei in each phase are identical; otherwise the relations between the observed and true parameters of the phases become more complex[27].

3. Derivation of Information about the Molecules in Complex Systems from NMR Data

Examination of Eqns. (3) and (5) shows that the derivation of information about the molecular characteristics of P–LMS systems is complicated and consists of several stages. In order to obtain the parameters describing the kinetic state of systems, it is usual to proceed via the following steps: (1) the magnetic parameters (T'_{1i}, T'_{2i}, p'_i, etc.), which generally speaking can differ from the true values characterising each phase, are measured; (2) a relation is established between the measured magnetic quantities and the kinetic units responsible for them (a segment of the macromolecule, its side groups, solvent molecules, etc.); (3) the true magnetic parameters of each phase (T_1, T_{2i}, p_i) are calculated from Eqns. of type (5*c*); (4) a definite relaxation mechanism, which establishes the type and characteristics of the motion of each kinetic unit, are attributed to the system; (5) the correlation times of the molecular motions of the polymer and low-molecular-weight substance are determined.

The first stage does not require explanation: it involves the measurement of the magnetic parameters, the values of which may be distorted by the exchange processes[28] occurring in the test systems (translational displacement of molecules from "phase" to "phase", spin diffusion, proton exchange, etc.). Since the systems considered are characteristic by several transverse and longitudinal relaxation times, the second stage of the treatment involves the assignment of the measured quantities to a specific kinetic unit whose motion determines a particular relaxation time. This process requires particular caution, since it can lead to an incorrect treatment of the results. For a more reliable assignment of the times to kinetic units, one of the system components (usually the solvent) is deuterated and ^1H and ^2D resonance is observed[29]. Next the true values of T_{1i}, T_{2i}, p_i, etc. are calculated from one of Eqns. (5) (third stage). After that, on the basis of general considerations or using additional information, a definite mechanism (dipole–dipole, quadrupolar, and spin–rotational interaction) is assigned to each relaxation time and the type of motion of the kinetic units and its characteristics (continuous rotation, jumps by large angles, etc., the presence of a spectrum of τ_c values) are specified. This makes it possible to select a definite relation between the correlation times of the motions and the magnetic relaxation times [see, for example, Eqn. (3)] and one can then calculate the values of τ_c (fifth stage). An example of the sequence of steps in the analysis of NMR data is provided by studies on adsorption systems[30] and polymer solutions[31].

The specific results obtained in recent years as a result of the applications of NMR to the study of systems in which we are interested are examined below.

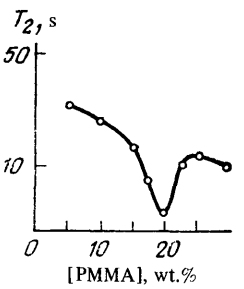


Figure 1. Concentration variation of T_2 for benzene in a solution of syndiotactic PMMA with a molecular weight of 2.2×10^6.[33]

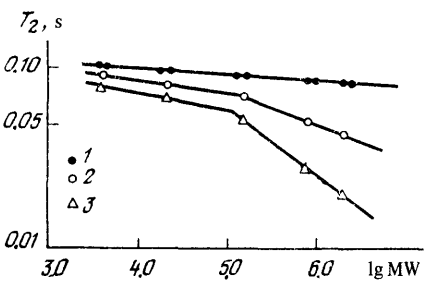


Figure 2. Variation of T_2 for the CH_3 group in the PIB–CCl_4 system with the molecular weight (MW) at 35°C; volume fraction of polymer: 1) 0.05; 2) 0.20; 3) 0.30.[34]

III. POLYMER SOLUTIONS

1. The Structure of the Solution

The measurement of the nuclear relaxation times of polymers yields information about the structure of solutions[4,32–34]. Thus the microscopic inhomogeneity of poly(methyl methacrylate) (PMM)—benzene systems has been investigated[33] and it was found that, depending on the polymer concentration, T_2 passes through a minimum (Fig. 1). The appearance of a minimum is a consequence of the diffusion of benzene molecules through the region of inhomogeneity of the solution. By means of a semiquantitative estimate of this effect, the authors found that the average size of the inhomogeneity is 200 Å, which roughly agrees with the radius of rotation of the polymer segment.

Characteristic breaks (Fig. 2), indicating the existence of a critical molecular weight or a critical concentration at which there is a sharp change in the properties of the system, have been observed in the study of polyisobutylene solutions (PIB) in CCl_4 on the curves relating T_2 to concentration or the molecular weight of the polymer [34]. According to the authors "hooked" formations are produced in the test solutions for polymer molecular weights and concentrations in excess of the critical values. It is suggested that these constitute the nodes of a fluctuation network made up of macromolecules and their supermolecular formations. The variation of local mobility, which determines T_2, with concentration is followed by observing the formation and density of this network.

The presence of empty cavities in concentrated solutions of atactic polystyrene in anisole, which are in a vitreous state, has been pointed out [35]. The LMS molecules in the cavities execute rotational and translational "jumps" at low temperatures. It has been found that LMS molecules then exhibit a tendency towards association [35,36]. The broadening of the ^{13}C NMR absorption lines in PIB solutions in CCl_4 [37] indicates a partial entanglement of the macrochains, which becomes more pronounced with increase of the molecular weight of the polymer and can be one of the causes of the formation of a three-dimensional network in solution.

The possibility of structural rearrangements in polymer solutions has been noted by Fedotov [38], who observed that the correlation time characterising the mobility of water molecules interacting with the macromolecules of poly(acrylic acid) (PAA) increases with increase of temperature from 10° to 80°C, while in a solution containing poly(methacrylic acid) (PMAA) it falls. The rearrangements are attributed to the uncoiling of the chains due to a redistribution of hydrogen bonds. It has also been found that the loose PAA macromolecule can be hydrated by twice as much water as the more rigid PMAA molecule. It is suggested that the presence of structures in macromolecules gives rise to steric hindrance to interaction between water and the macromolecule.

An attempt has been made to determine the fraction of macromolecules in helical and coiled conformations in aqueous solutions of serum albumin. [39,40] However, it is believed [41] that the information obtained in these studies [39,40] about the conformations of hydrated protein macromolecules is doubtful. Outhred and George [41] explained the same experimental results by assuming that the motion of the polymer macromolecules in solution is characterised by a spectrum of correlation times with a maximum at $\tau = 10^{-9.3}$ s.

Additional information about the structure of solutions has been obtained by studying the self-diffusion coefficient of both LMS molecules and macromolecules in aprotic solvents [42,50]. The results are usually interpreted by means of Fujita's free volume theory [51]. The parameters characterising the size of the "critical" regions for diffusional motion in solutions of natural rubber (NR), PIB, polystyrene (PS), and PMMA have been determined [42-44]. It was established that (1) in translational motion the greatest disruption of the packing of solvent molecules in the vicinity of macromolecules is observed for rigid-chain polymers and (2) that the self-diffusion of LMS molecules takes place as a result of the interchange of the kinetic units of the polymer and whole groups of solvent molecules.

A study of the self-diffusion of LMS in the PS–benzene and PS–cyclohexane systems showed [45] that the minimum free volume necessary for "jumps" by solvent molecules is greater by a factor of approximately 1.5 in the second system compared with the first. Analogous data have been obtained for PMMA solutions in benzene and acetone. [46] The temperature dependence of the free volume has been studied for these solutions and the coefficient of the expansion of the free volume in PMMA has been determined.

The study of D_S of the solvent with increasing concentration of polymers (PMMA, PS) [45,46] suggests the formation of cavities within entangled macromolecules which LMS molecules enter and are trapped. The cause of the inhibition of the translational motion of small molecules is believed to be [45,46,50] the formation of short-lived globules and small cavities in which solvent molecules are accommodated. Kosfeld and Goffloo [45] concluded that the self-diffusion of solvent molecules is determined by the motion of the macromolecules. The nature of the concentration variation of D_S for macromolecules permits a number of conclusions concerning the distribution of macromolecules in solution [42,44,47].

2. Estimation of the Quality of the Solvent

The quality of the solvent has a significant influence on the intermolecular interaction of the components in polymer solutions, which determines the molecular mobility. Since T_1, T_2, and D_S depend on the latter, the measurement of nuclear magnetic characteristics makes it possible to infer the quality of the solvent.

The first conclusions about the quality of the solvent based on the analysis of T_1 were put forward [52] in relation to the study of dilute PIB solutions in "good" (CCl_4) and "poor" (C_6D_6) solvents over a wide range of temperatures and polymer molecular weights. Comparison of the T_1 values for specimens corresponding to equal fractions of the solvent shows that relaxation in a good solvent is faster than in a poor one. It was also found that a minimum in T_1, caused by the rotation of the CH_3 group of the polymer, lies at a temperature 25°C lower in a good solvent than in a poor solvent and its value is smaller in the latter case. This finding apparently shows that the conformations of macromolecules in a good solvent are such that they give rise to less steric hindrance to the rotation of CH_3 groups.

It was later found that [53,54] the quality of the solvent has a similar influence on the intramolecular mobility also in moderately concentrated solutions. This conclusion was reached in a study of the temperature and concentration variation of the relaxation times T_1 and T_2 for PS and PMMA solutions in the aprotic solvents C_2Cl_4, C_6D_{12}, etc. Tanner et al. [47] observed that the translational motion of poly(ethylene oxide) macromolecules with a low molecular weight (approximately 1000) in a good solvent ($CDCl_3$) is more vigorous than in a poor solvent (CCl_4), while in the case of large macromolecules (with a molecular weight of approximately 870 000) the opposite relation holds. This has been explained [47] by taking into account the influence of the viscosity of the solvent and also of the solvation and shape of the macromolecules in solution.

3. The State of Solvent Molecules

The state of CH_2Cl_2 molecules in a solution of atactic PS in which the volume fraction of the solvent was 0.10 to 0.24 has been investigated [55]. The system is characterised by a weak P–LMS interaction. The calculated correlation

times of the solvent molecules surrounded by similar molecules (τ_{SS}) and in the vicinity of macromolecules (τ_{SP}) showed that $1 \leqslant \tau_{SP}/\tau_{SS} \leqslant 2$. According to the author[55], this showed that there is only one type of environment for LMS molecules in a PS–CH_2Cl_2 solution and that it is impossible to distinguish the "free" and "bound" solvent species. The inhibition of small molecules is more effective in a polymer with a larger molecular weight. The increased "lifetime" of the CH_2Cl_2 molecule in the "trap" with increase of the polymer concentration is caused exclusively by the influence of the macromolecular chains and not some special interactions between the π-electron system of the benzene ring and the CH_2Cl_2 molecule.

The state of solvent molecules in dilute polymer solutions has been thoroughly investigated[31,56-59]. Solutions with a strong intermolecular interaction (hydrogen bonds) were examined; the temperature and concentration variations of the nuclear spin–lattice relaxation times T_1 for protons, deuterons, and chlorine nuclei were investigated and the self-diffusion coefficients were measured. The behaviour of the solvent can be described with the aid of a simple model with two states:

$$A + M \rightleftarrows AM,$$

where the solvent molecule A can be either in a free state or in a bound state (as a solvate AM combined with the macromolecule M). It has been established for solutions of polyvinylpyrrolidinone (PVP) in chloroform, where a hydrogen bond is formed between the carbonyl group of the pyrrole ring and the deuterium atom of chloroform, that the "lifetime" of the hydrogen bond ($\sim 5 \times 10^{-11}$ s) is long compared with the rotational correlation time of the molecules of pure chloroform ($\sim 10^{-12}$ s), but is very short compared with the fastest motion of the macromolecule ($\sim 10^{-9}$ s).[31] In a PVP–pyrrole solution[59] the "lifetime" of the hydrogen bond is approximately twice as long as the lifetime of the corresponding bond in the PVP–chloroform system. The reorientation of the pyrrole ring about the C–H bond in the complex with the polymer is retarded by a factor of 10 compared with the reorientation of pure pyrrole, while the rotation of chloroform molecules in the complex with PVP is retarded only by a factor of 3. According to the authors, the "lifetime" of the hydrogen bond can be regarded as the "lifetime" of the polymer–solvent solvate.

Comparison of the results of studies on PS solutions in methylene dichloride[55] and of PVP in $CDCl_3$ [31] showed that the state of solvent molecules is determined to a large extent by the extent of the interaction between the polymer and LMS molecules. In systems with a strong interaction between the components there is a possibility of the subdivision of molecules into "bound" and "free".

The study of proton and deuteron relaxation in PMMA–benzene solutions[57] showed that, in the absence of a strong polymer–solvent interaction, the "lifetime" of the bond between the components is of the same order of magnitude as the rotational correlation time of the benzene molecule. At the same time the translational correlation time of benzene ($\sim 10^{-10}$ s) is longer almost by two orders of magnitude than the rotational correlation time.

As was to be expected, an increase of the polymer concentration in the solution leads to a decrease of the rotational and translational mobilities of the LMS molecules.[43,44] It is striking that the inhibition of the molecules, characterised by the ratio D_S/D_{S0}, depends very little on the nature of the polymer or on the type of LMS (Fig. 3). Nevertheless it is claimed[43] on the basis of a study of D_S for H_2O, CH_3COOH, CH_3OH, and CH_2Cl_2 molecules in PVP solutions that the stronger the polymer–solvent interaction the greater the inhibition of the [mobilities of the] latter.

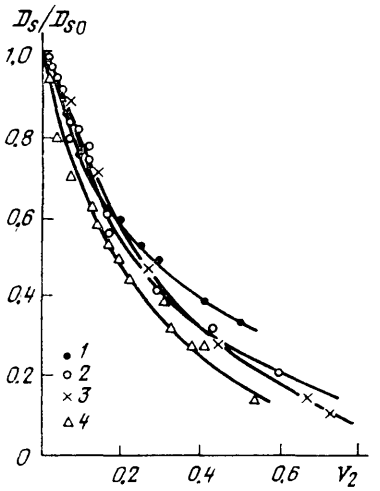


Figure 3, Dependence of the ratio of the self-diffusion coefficient of the solvent D_S in solution to the self-diffusion coefficient of the pure solvent D_{S0} on the volume fraction of the polymer in different systems: 1) natural rubber–benzene; 2) PIB–benzene; 3) PIB–toluene; 4) PMMA–toluene.[44]

The inhibition of [mobilities of] acetone molecules in solutions containing between zero and 20 wt.% PMMA has been studied over a wide temperature range[60] by the method of ^1H and ^{13}C spin–lattice relaxation. It was observed that the introduction of up to 10 wt.% of the polymer does not affect the translational and rotational diffusion of acetone molecules, but in the presence of 20 wt.% of the polymer the mobility decreases sharply. The sharp inhibition [of mobilities] of the solvent molecules over a narrow concentration range can be explained by the formation of an entangled network of macromolecules.

4. The Study of Selective Solvation

An independent field of research on complex formation in polymer solutions by NMR involves the study of the selective solvation by the polymer of one of the components in a mixture of two solvents[29,61-64]. The mixtures are chosen so that one component is a good solvent and the other a poor one. Liu observed for the first time[61] in a study of T_1 for the PIB + CCl_4 (C_6H_{12}) + CH_2Cl_2 and PMMA + CCl_4 + CH_3COCH_3 (CH_2Cl_2) systems that the spin–lattice relaxation time of one of the components of the mixture of solvents depends strongly on the type of added polymer, i.e. that the interaction of the polymer with this solution component is stronger than with the other one. In the systems indicated above CH_2Cl_2 is a good solvent for PMA but a poor one for PIB.

The study of the spin–lattice relaxation of C_6H_6 + C_6H_{12} + PS, C_6H_6 + CCl_4 + PMMA, $CHCl_3$ + CCl_4 + PMMA, and C_6H_6 + $CHCl_3$ + PMMA mixtures[62] with different ratios of the LMS components at a constant polymer concentration established that in mixtures with PS benzene (a good solvent) is solvated preferentially and that the polymer monomer unit combines with four C_6H_6 molecules. The numbers of benzene and chloroform molecules adsorbed on the PMMA monomer unit are respectively 5 and 4.

In solutions of PVP [29] in a mixture of solvents consisting of $CHCl_3$ (a good solvent) and C_6H_{12} (a poor solvent) the inhibition of the rotation of $CHCl_3$ molecules was observed as the polymer content was increased, while the mobility of C_6H_{12} remained unchanged. This finding can be explained by the preferential solvation of PVP by $CHCl_3$. Anallgous preferential solvation of PS by $CHCl_3$ had been observed in PS + $CHCl_3$ + CH_3COCH_3 mixtures[29].

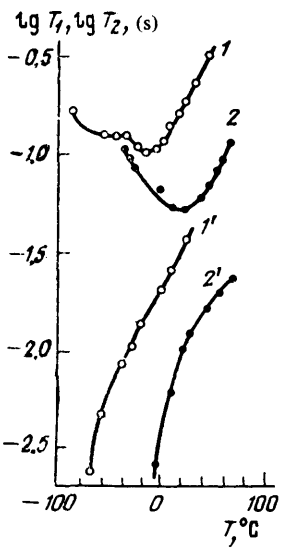


Figure 4. Temperature variation of $\lg T_1$ (curves *1* and *2*) and $\lg T_2$ (curves *1'* and *2'*) for solutions of PS in $C_6D_6CD_3$ at concentrations of 5 wt.% (curves *1* and *1'*) and 40 wt.% (curves *2* and *2'*).[53]

A novel approach to the study of the solvation equilibrium in a system with a mixed solvent, namely CCl_4 + PMMA + C_6H_6, at 31°C in the polymer concentration range from 0 to 100 g litre^{-1} has been described[63,64]. The author introduced the equilibrium constant K for the exchange of solvent molecules, which depends on the concentrations of molecules of both solvents—free and involved in solvate complexes with the polymer. In order to determine K, use was made of the measured T_1 for benzene protons at different polymer concentrations. It was found that in the system indicated above the exchange equilibrium constant obtained is $K = 2.5 \pm 0.5$; on the other hand, $K = 0$ in the C_6O_6 + PMMA + C_6H_6 system, where there is no selective solvation. Thus K is a convenient measure of the preferential solvation of one component (C_6H_6).

5. Phase Separation in Solutions

Information about the intermolecular interactions under conditions preceding the separation of the solution into layers has been obtained[53] in a study of PS solutions in aprotic solvents (CCl_4, $CDCl_3$, $C_6D_5CD_3$, and C_6D_{12}) at different concentrations. The amount of polymer was varied from 5 to 40 mole % and its molecular weight was varied from 10^4 to 10^6. The temperature variation of T_1 and T_2 for PS solutions in $C_6D_5CD_3$ is illustrated in Fig.4. The authors suggest that the stepwise variation of T_1 reflects the change in the state of the macromolecules, which involves the appearance of long-lived polymer–polymer contacts (associated species, aggregates), i.e. the separation of the solution into layers. Under these conditions, the observed relaxation time T_1 is a weight-average quantity referring to protons, highly mobile macromolecules, and macromolecules inhibited by the appearance of long-lived interchain contacts.

It has been observed[52] that the time T_2 in dilute solutions also changes when phase separation begins.

6. Characteristics of the Motion of Macromolecules

The mechanisms of the motion of PIB macromolecules in aprotic solvents have been investigated[52] and two forms of macromolecular motion have been found: (1) the low-temperature form involving the reorientation of the CH_3 groups and (2) the high-temperature form involving segmental motion. The addition of a low-molecular-weight substance facilitates the rotation of the CH_3 groups, whose motion is not free in the pure polymer.

The analogous problem of the study of the local forms of motion (rotation of CH_3 groups and reorientation of the Si–C bond) of macromolecules has been solved[65] in relation to solutions of PDMS [polydimethylsiloxane] having different molecular weights in protic (C_6H_6, C_6H_5Cl) and aprotic (C_6D_6, C_6D_{12}, CCl_4) solvents. The polymer concentration in solution varied from 1 to 20 g in 100 ml of the solvent. It is assumed that the inhibition of the rotation of the CH_3 groups increases with increasing molecular weight of the polymer at fairly high concentrations of the latter owing to steric hindrance.

In solutions of poly(ethylene oxide) in HCl, H_2O, D_2O, and DCl and pentachloroethane ($CHCL_2CCl_3$) the motions associated with conformational transitions around C–C bonds were investigated[66]. It was noted that the rotation of the molecule as a whole influences the relaxation in low-molecular-weight oligomers only, i.e. the mechanism of the motion of macromolecules changes from segmental to the rotation of the molecule as a whole as the molecular weight decreases.

The influence of the molecular weight of the polymer on the degree of inhibition of the translational motion of solvent molecules has been demonstrated[42,44,49]. New possibilities for the study of macromolecular motion arise in connection with the ^{13}C NMR method[37,67–73]. It has been observed that the motion of the carbon chain is almost isotropic in a 20% solution of PIB in $CDCl_3$.[37] The study of PS–tetrachloroethylene solutions at the same concentration showed that the rotation of the phenyl groups of the polymer is subject to a considerable steric inhibition, because their correlation time is appreciably longer than the effective correlation time for segmental motion[67]. It has been established that macromolecules with low molecular weights move as a whole and that these motions determine the observed T_1, while macromolecules with

high molecular weights exhibit predominantly an internal (segmental) motion of the polymer chain, which is fairly rapid[64-73].

Comparison of the activation energies for segmental motion in polyethylene (PE), polypropylene, and PIB solutions in *o*-dichlorobenzene showed[37] that the activation energy E increases on passing from PE to PIB. This is due to steric hindrance to the motion of methyl groups when the latter are introduced into the polymer as side units. The study of the relaxation of ^{13}C nuclei showed[73] that the motion of poly(propylene oxide) (PPO) molecules and PIB with a molecular weight of 2500 in $CDCl_3$ depends on the frictional forces acting from the side of the immediate environment. According to the author[73], the immediate environment consists of the first solvation shell, which is believed to be formed when the ratio of the number of $CDCl_3$ molecules to the number of monomer units is 5. It was established that the motion of CH_3 groups of PIB is strongly inhibited and that their orientation takes place co-operatively with neighbouring methyl groups. It is claimed that in PPO and PIB solutions, where the ratio of the number of solvent molecules to the number of monomer units exceeds 5, the correlation of the motion of the main chain disappears over a distance equal to 2–3 monomer units.

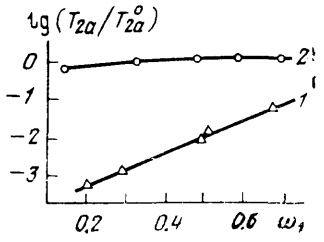


Figure 5. Dependence of $\lg (T_{2a}/T_{2a}^0)$ on the weight fraction ω_1 of the plasticiser in different systems: 1) PVC–DBP; 2) PVC–glycerol (at room temperature) [24].

IV. PLASTICISED POLYMERS

Plasticised polymer systems differ from solutions by the high content of the polymer and the consequent very high viscosity. The difficulty of the study of such objects by NMR is due to the fact that the plasticisers usually employed are high-boiling liquids whose molecules are bulky, have a complex structure, and possess a large number of internal degrees of freedom; the deuteration of such molecules is usually difficult. However, a series of results have been obtained recently showing the usefulness of NMR, particularly its pulsed version, in the study of such systems.

It has been established[24] that, from the standpoint of NMR, plasticised polymers are multiphase systems where exchange between the phases as a rule does not occur or is fairly slow. In this case the study of the decrease of transverse magnetisation[74], from which the nuclear relaxation time T_1 is determined by Eqn.5*b*, is most informative. Specimens with a moderate content of the plasticiser (up to 80 wt.%) are described by two times T_2 over a wide range of temperatures: a long time T_{2a} and a shorter time T_{2b}. The former characterises mainly the plasticiser protons and the latter the polymer protons[75].

1. Assessment of the Nature of the Plasticisation of Polymers

In the first studies[76,77] on plasticised PVC by the pulsed method it was shown that at room temperature T_{2a} for a molecular plasticiser introduced into the polymer is smaller by 2–3 orders of magnitude than T_{2a}^0 for the pure plasticiser, while in a polymer plasticised by a structural plasticiser $T_{2a} \simeq T_{2a}^0$. This feature makes it possible to deduce the type of plasticiser directly from the measured transverse relaxation time.

The concentration variation of $\lg (T_{2a}/T_{2a}^0)$ for a molecular plasticiser (Fig.5) is described by the equation[24]

$$\lg [T_{2a}/T_{2a}^0] = A\omega_1 + B$$

where ω_1 is the weight fraction of the plasticiser and A and B are constants which depend on the nature of the polymer–plasticiser interaction (high values of A and low values of B correspond to a strong interaction and low values of A and high values of B correspond to a weak interaction). In many systems (for example, in PVC plasticised with glycerol, ethyl stearate, castor oil, phthalates, and sebacates) the form and positions of the curves corresponding to this relation make it possible to determine the limits of the compatibility of the polymer and plasticiser and to introduce criteria for subdividing plasticisers into molecular and structural[78,79].

Analogous results were obtained for plasticised PS and polyvinylbutyral[80], which demonstrates the applicability of the parameter T_{2a}/T_{2a}^0 to the estimation of the nature of the plasticisation for a wide range of polymers. The characteristics of the plasticisation of vinyl chloride–vinyl acetate copolymers by phthalates have been investigated[81,82]. Thus dioctyl phthalate (DOP) is a molecular plasticiser for PVC and a structural plasticiser for poly(vinyl acetate). Examination of the concentration variation of T_{2a} made it possible to assess the compatibility of DOP with copolymers and to observe an inversion of the action of the plasticiser (a transition, depending on the content of vinyl acetate groups, from the molecular to the structural mechanism of plasticisation).

A broad-line NMR study of the nature of the polymer–plasticiser interaction in relation to rubbers plasticised by phthalates and sebacates has been undertaken[83]. The difference between the second moments of the absorption lines of the plasticised specimen, on the one hand, and the pure polymer and plasticiser taken in appropriate proportions, on the other, served as a characteristic of the interaction.

2. The Introduction of the Plasticiser into the Polymer

Measurements of T_{2a} make it possible to investigate the processes involved in the combination of the plasticiser with the polymer in the mixing and rolling stage, i.e. pulsed NMR can be used for purely technological purposes[80,84]. Thus the optimum time t_m for the mixing of PVC with phthalates and sebacates at 98°C in order to obtain a homogeneous mixture has been estimated (Fig.6). The time t_m was determined from the point of intersection of the tangents to the sharply descending and horizontal sections of the T_{2a}—mixing time curves. The mixing time

t_m increases for all plasticisers with increase of their concentration. It is a minimum for systems which are highly compatible. An analogous approach has been used to estimate the optimum rolling time for films of plasticised PVC. It was established [84] that, with increase of the temperature of the operation, the rolling time required for the preparation of homogeneous films diminishes. Analogous results have obtained in the study of the pressing of PVC specimens [80].

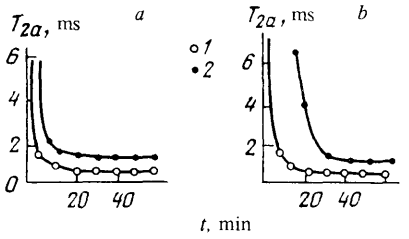


Figure 6. Dependence of T_2 on the mixing time of the components at 98°C for PVC–DBP (*a*) and PVC–DOP (*b*) systems containing 40 wt.% (curves *1*) and 50 wt.% (curves *2*) of the plasticiser [84].

3. The State of Plasticiser Molecules Introduced into the Polymer

The main aim of the plasticisation of polymers is to create the maximum molecular mobility in the polymer–plasticiser system [85]. It is therefore of interest to investigate the nature of the motion of small molecules introduced into the polymer, particularly since plasticiser molecules constitute a kind of "label" characterising the system as a whole[24].

(a) Plasticised PVC. The PVC–phthalate system with a low polymer content (< 10 wt.%) belongs to gels of type 1B.[1] However, at high PVC concentrations (> 50 wt.%) they can be treated as ordinary plasticised systems.

Measurements of the spin–lattice relaxation times in PVC plasticised by various phthalates and nitrophthalates in the range from −150°C to +70°C [86,87] made it possible to determine the nature of the motion executed by small molecules: the methyl groups are seen to rotate between −150°C and −120°C, while at approximately −50°C alkyl groups rotate as a whole at a frequency of approximately 10^7 Hz regardless of the concentration of the added plasticiser. However, a complete interpretation of the temperature variation of T_1 in such systems is difficult, since the measured quantities are as a rule distorted by exchange [74]. The study of the temperature variation of the transverse relaxation times proved to be more informative in this respect.

In the region of moderate plasticiser concentrations (≤ 60 wt.%) the PVC–DMF and PVC–DOP systems [74,75] are characterised, as mentioned above, by two relaxation times (Fig. 7). It was established that T_{2a} is determined by the rotational motion of the plasticiser molecules. The decrease of T_{2a} with increasing content of the polymer in the system relative to T_{2a}^0 over the entire experimental temperature and concentration ranges indicates a reduction of the rotational mobility of the phthalate molecules introduced into PVC. It has been noted that in the specimens investigated there is a distribution of correlation times for the reorientation of molecules. This makes it possible to regard the entire plasticiser introduced into the polymer as "bound" to different extents, provided that the degree of "binding" is estimated in terms of the degree of retardation of the rotational motion. The most probable correlation times for the rotational (τ_{r_0}) and translational (τ_t) motions of DMF molecules have been estimated.

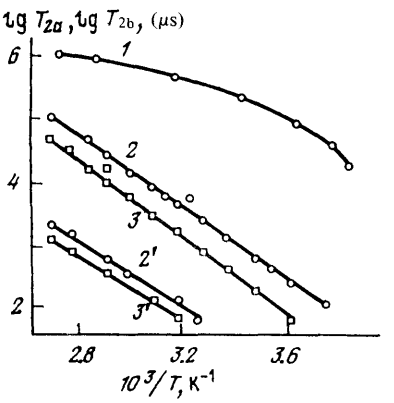


Figure 7. Temperature variation of lg T_{2a} (curves *2* and *3*) and lg T_{2b} (curves *2'* and *3'*) for PVC–DMF systems containing 24.2 mole % DMF (curves *2* and *2'*) and 13.3 mole % DMF (curves *3* and *3'*). Curve *1*—pure DMF. [75]

The NMR method permits a sounder approach to the determination of the lifetime of the polymer–plasticiser solvate. Thus in the PVC–DMF system it is most useful to select as the lifetime the correlation time τ_{r_0} for the rotational motion as the shortest time parameter characterising the system. However, since the correlation times for reorientations are characterised by a spectrum of values, one must assume that the lifetimes of various solvates present are different and have a wide range of values, which depend on the content of the plasticiser and the temperature of the measurement.

It has been established that the phthalate molecule interacts with the polar group of PVC, undergoes a reorientation during a period $\tau_t \geq \tau_r$, and then "jumps" to another site where it begins to rotate, etc. The PVC–dioctyl sebacate system has been investigated [88].

(b) Plasticised nitrocellulose. A study of the characteristics of the molecular motion of trinitroglycerol (TNG) plasticising nitrocellulose (NC) has been described [89]. Only T_{2a} was measured by high-resolution NMR. Various nitrocelluloses with nitrogen contents varying from 10.9 to 13.9 wt.% were investigated; the TNG concentration was in the range 30–60 wt.%. The solvation limit, which depends on the nitrogen content in NC, was estimated. The degree of nitration of cellulose was shown to influence the mobility of the plasticiser molecules. The linear relation between lg T_{2a} and $1/T$ makes it possible to determine the activation energies for

the motion of TNG. The values of E proved to be independent of the plasticiser content.

The analogous NC–TNG systems have been investigated[75,90] by pulsed NMR. Like the PVC–phthalates specimens, the above systems are characterised by two transverse relaxation times. The presence of a spectrum of correlation times for the motion of TNG molecules at $T < 60$°C was demonstrated. The pressure of a plateau on the $\lg T_{2a} = f(1/T)$ curves in the region of $T \geqslant 60$°C (Fig. 8) indicates the occurrence of exchange between the "quasi-free" and "bound" plasticiser species under these conditions. The rate of molecular exchange was estimated as ~10–10^2 Hz. The molecular motion in polystyrene plasticised by dibutyl phthalate has been investigated[91].

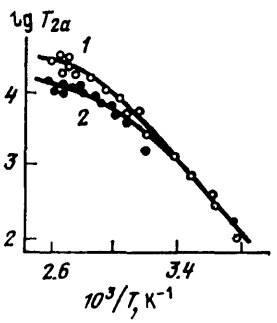


Figure 8. Temperature variation of lg T_{2a} for low-nitrogen (curve *1*) and high-nitrogen (curve *2*) nitrocellulose containing 50 wt.% of trinitroglycerol.[90]

The dynamic picture of the state of phthalate molecules introduced into PVC makes it possible to represent the overall picture of the transition of the plasticised system from the vitreous to the viscoelastic state. This transition is accompanied by a kind of "accelerated rocking" of the polymeric skeleton under the influence of the intense rotational and translational motion of the plasticiser molecules. The efficiency of this rocking depends on the number of internal degrees of freedom f of the plasticiser molecules and the amount of plasticiser. The condition for vitrification can be formulated as follows in this case:

$$\alpha f T_g \frac{Nm}{1-N} = E_p,$$

where N is the molar percentage of the plasticiser, m the number of monomeric units in the segment, E_p the minimum energy required to initiate segmental motion, α the proportionality coefficient, and T_g the glass point.

Ideas concerning the mobility of nitrocellulose macromolecules in plasticised specimens have been put forward[93].

V. THE GEL STATE OF POLYMERS

In the study of gels NMR has been used recently mainly to investigate aqueous polymer gels (agarose, gelatin, starch, carboxymethylcellulose, etc.). With some exceptions, the term LMS will therefore be understood below to imply water.

The majority of studies were carried out by pulsed NMR, gels containing a small amount of the polymer (2–3 wt.%) being characterised by unique values of T_1 and T_2 [94,95] or a one-component NMR absorption curve[96]. For a polymer content exceeding the above limit, there is a two-component absorption line. The broad component ($\delta \simeq 9$ Oe) is attributed to the polymer protons and the narrow component to the water protons[97].

1. The Formation, Fusion, and Ageing of Gels

Gels are known[98] to be characterised by gel (T_{gel}) and melting (T_m) points. The dependence of T_2 on the age of an aqueous agarose solution for T less than the gel melting point (Fig. 9) makes it possible to follow the gel formation process[95]. The curves illustrated in Fig. 9 suggest that an increase of the agarose content increases the rate of gel formation; the authors attribute this to the intensification of the nucleation stage. The decrease of T_2 in the course of the formation of the gel (Fig. 9) is accounted for by the decrease of the mobility of the macromolecules and of bound water. The T_2–agarose concentration curves indicate the formation of a macromolecular network. The temperature variation of T_2, measured in the course of the cooling of the specimen (curve *2'*, Fig. 10), shows a sharp break in the region of $T \simeq T_{gel}$ due to the loss of molecular mobility in the system. It is noteworthy that the $T_1(T)$ relations do not exhibit such anomalies. The decrease of T_2 with the duration of storage of the gel suggests the "ageing" of the system. Even a 3% solution of agarose at 40°C, i.e. above T_{gel}, "ages" in the course of 6 h without any visible signs of the formation of a network (T_2 diminishes).

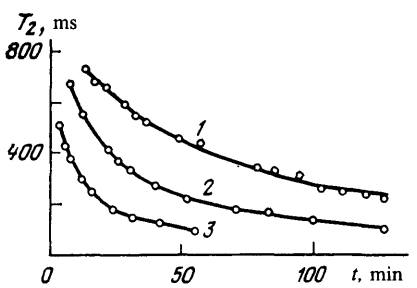


Figure 9. Dependence of T_2 on the gel formation time t at 34.7°C for different concentrations of agarose in solution (%) [95]: 1) 1.6; 2) 2; 3) 3.

The formation of the gel in a 0.5% solution of monodisperse α-gelatin with a molecular weight of 110 000 has been investigated[99]. The integral intensities J of lecithinyl, alanyl, prolyl, and arginyl lines were determined by high-resolution NMR in the course of the formation of the gel at 15°C. The form and positions of all the observed lines remain unchanged during the process, but the values of J diminish in accordance with the law

$$\frac{dJ}{J} = -K\,dt$$

with the same constant K for all the lines.

The decrease of J is attributed to the formation of helical molecules in which there is a sharp retardation of molecular motion, which entails a broadening of the line, precluding the possibility of its observation by high-resolution NMR. The same view has been expressed by Rouse and Gross[100]. This enabled Finer et al.[99] to reach conclusions about the possible conformational changes undergone by α-gelatin on formation of the gel. It is believed that gel formation is a multistage process in which the slow stage is described by the equation quoted above and involves the formation of the nuclei of the helix from the coil.

Gel formation in the poly(hexadecyl acrylate)–n-decane system has been investigated[101] with a polymer concentration varied from 1 to 100%. It was shown that at the temperature T_{gel} there are anomalies in the behaviour of T_1, the effective T_2, and the self-diffusion coefficient D_S. It was established that the formation of the gel is accompanied by a decrease of the mobility of the polymer molecules — the retardation of the rotational and translational motion of the molecules of the bound and non-solvated solvent.

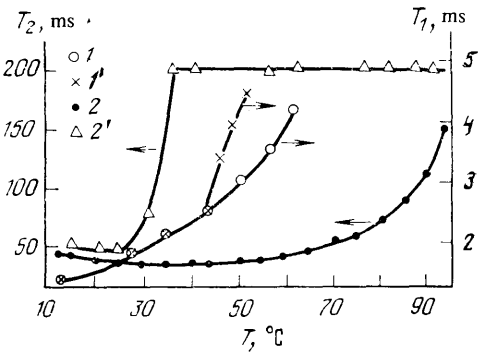


Figure 10. Temperature variation of T_1 obtained on heating (*1*) and cooling (*1'*) a 5% agarose gel and temperature variation of T_2 on heating (*2*) and cooling (*2'*) a 2% agarose gel.[95]

2. Hysteresis Phenomena in Gels

Hysteresis in agarose gels[94,95] consists in different positions of the curves representing the temperature variation of T_1 and particularly T_2 measured during the cooling and heating of the system (curves *1* and *1'* and *2* and *2'* in Fig. 10). It has been shown[95] that the form of the hysteresis loop depends on the maximum temperature to which the test specimen was heated during the measurement. The causes of the hysteresis have not been discussed, but presumably this effect is associated with the kinetic nature of the curves obtained. Another type of hysteresis is observed in the measurement of T_2 in a 3% agarose solution with alternation of the specimen heating and cooling cycles (Fig. 11).[95] The authors suggest that, with increase of temperature, the existing nodes break down and the mobility of the chains increases; however, on cooling to 60°C the nodes are restored to a different extent in each case, which leads to hysteresis.

3. The State of Water in Gels

Earlier studies (without the use of NMR) of the behaviour of water in gels led to the conclusion that the majority of water molecules are in a state intermediate between that of ordinary water and ice[102,103]. However, systematic study of the agarose–water system by NMR showed[94,104] that "free" water, having the mobility of ordinary bulk-phase water and "bound" water predominate in the gels. The degree of "binding" of water can be different and Sterling and Masuzawa[96] divided bound water into two parts: (1) simply "bound" water whose molecules exhibit a limited mobility and (2) "solid" water. Aizawa et al.[97], who investigated agarose gels in which the polymer content was varied within wide limits (from zero to 100%), suggest that the form of the curve for the concentration variation of the NMR absorption line width δ (Fig. 12) makes it possible to differentiate, apart from "free" and "bound" water, also a third type, namely "intermediate" water. Point A (Fig. 12) permits the determination of the amount of "bound" water. The independence of δ of polymer concentration along section AB indicates the existence of "intermediate" water, whose introduction is particularly necessary in the treatment of dilatometric and electrochemical data in such systems[105]. The sharp increase of δ in the region of 0°C indicates the existence of free water. Whereas bound water consists of molecules strongly interacting with the OH groups of agarose, the nature of the intermediate water is not clear.

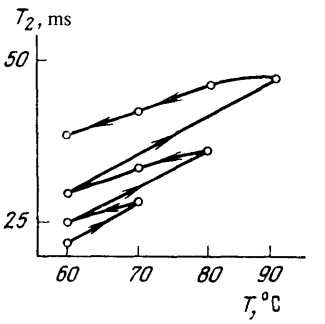


Figure 11. Temperature variation of T_2 for a 3% agarose solution recorded in the course of heating–cooling cycles.[95]

The use of pulsed NMR made it possible to determine the fraction of free water in gels (on the assumption that free and bound water exist in the system). Thus, a study of agarose gels containing 1–8 wt.% of the polymer showed[94] that more than two-thirds of the entire water is present in the free state. This is indicated by the closeness of the values of D_S for the water in gels ($D_S = 1.95 \times 10^{-5}$ cm^2 s^{-1}) and for pure water ($D_S = 2.25 \times 10^{-5}$ cm^2 s^{-1}) at room temperature. In the next study by the same authors[104], where a mixture of H_2O and D_2O with different component ratios was used as the solvent for agarose, it was shown that only 1% of the entire water is present in the bound state, in the gel containing 7–8 wt.% of agarose, while the remaining 99% is ordinary free water. With increase of polymer concentration, the fraction of bound water increases. Attention has been drawn to the small

difference between the values of D_S determined by NMR and the tracer atom method, which apparently indicates the existence in gels of "barriers" (various macromolecular structures) distributed at comparatively long distances from one another. A later study[106] established that 1 g of agarose retains 0.59 g of water, which is several times more than the amount of bound water determined by Woessner and Snowden[104]. However, the scheme proposed by Derbyshire and Duff[106] for the interpretation of relaxation data yields many anomalous results, which are difficult to explain from a physically significant standpoint.

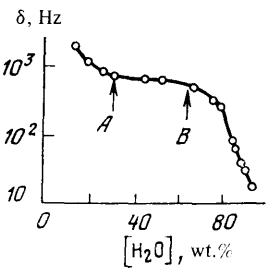


Figure 12. Dependence of the NMR absorption line width δ on the water content in agarose gels at 25°C.[97]

Ideas concerning the state of bound water have been put forward. In particular, it has been shown[104] that the rotational motion of its molecules should be anisotropic. At $T > 75$°C the bound molecules begin to rotate more vigorously, which can lead to the disruption of the water–agarose hydroxyls solvate. Agarose gels have been investigated[107] in the temperature range from −10° to −80°C, where free bulk phase water is frozen and the bound water exhibits some mobility (down to −80°C). The form of the temperature and concentration variations of T_1 permits the conclusion that the molecules of bound water have a different mobility and that their behaviour requires the introduction of a logarithmic normal distribution of the correlation times[108] for molecular motion.

VI. LOW-MOLECULAR-WEIGHT SUBSTANCES ADSORBED ON POLYMERS

1. The Interaction of Adsorbed Molecules with the Polymer

A few studies have been devoted to the NMR investigation of the adsorption of LMS by polymers. In most of them the substance adsorbed by the polymer was water. Thus a study has been made[109] of the interaction of H_2O molecules with oriented nylon 6,6 macromolecules. It was noted that the narrow component in the spectrum, corresponding to the molecules of adsorbed water, appears for a water content in excess of 1.4 wt.% and that its form is independent of the angle between the axis of the fibre and the direction of the magnetic field. For higher percentage moisture contents, water molecules decrease by 20–30°C the temperature of the transition associated with the motion in the crystalline regions of the polymer and lead to the appearance of a water phase with an intermediate mobility, due to motion in the amorphous parts of the polymer, and the "free" water phase. A study of the temperature variation of T_1 and T_2 in a polystyrene latex showed[110] that the presence of water decreases T_g for the polymer particles approximately by 10° and that its influence is somewhat greater in the presence of a concentrated electrolyte (0.1 M manganese sulphate). It has also been found that the penetration of the electrolyte into the polystyrene particles is restricted by a thin layer having a thickness of approximately 1 nm.

The interaction of adsorbed molecules with the polymer depends appreciably on its crystallinity[111]. The same conclusion was arrived at by the analysis of the temperature variations of the relaxation times for various celluloses. It has been found that the barrier to the diffusion of water molecules in cellulose of low crystallinity and based on cotton fibres is lower than in highly crystalline specimens.

The influence of ionic salts on the interaction of water molecules with collagen has been examined[112] on the basis of a ^2H NMR study. The decrease of the deuteron quadrupole splitting due to adsorbed water molecules in the presence of salts indicates a decrease of the fraction of water molecules bound to collagen fibres by hydrogen bonds. It is suggested that ions should either block certain sections of the chain, suitable for the formation of hydrogen bonds, or should alter slightly the conformation of the collagen molecules, hindering the binding of water.

Analysis of the NMR data for hydrated and oriented collagen fibres [113,114] suggests that water molecules diffuse rapidly between the polymer fibres. This motion is slightly anisotropic.

The study of the relaxation behaviour of water molecules adsorbed on keratin led to the hypothesis[115] that water molecules form clusters, whose number increases with increasing water content in the specimens. It has been established that water molecules have a continuous spectrum of correlation times for their motion and that, with increase in the amount of moisture in the specimens, the width of the spectrum diminishes.

In hydrated collagen only some of the adsorbed water molecules are linked to the collagen triple helix and are oriented. The remaining ("free") molecules are in a state of rapid reorientation. There is rapid exchange between the bound and free molecules. Examination of the NMR spectra led Fung and Traumann[112] to the same conclusion. It is believed that, in the presence of high water contents, excess water appears and is distributed on the surface of the specimen where it does not participate in exchange with water within the bulk of the specimen.

It has been reported[116] that 0.05–0.3 of all the cellulose protons are involved in exchange with water protons in celluloses or purified paper fabrics, silk yarn, and artificial silk in the presence of 7% of water.

The study of water adsorbed by specimens of cellulose acetate with different degrees of substitution at 20°C and a water concentration of approximately 10% showed[117] that the mobility of water molecules passes through a maximum for degrees of substitution in the range 0.5–0.6. The change in the mobility of water molecules is caused by redistribution of hydrogen bonds.

The NMR method makes it possible to determine the amount of water bound to the polymer. Thus it has been found[118] from ^2H NMR spectra that in oriented collagen fibres 1 g of the polymer binds 0.6 g of heavy water. The amount of water in celluloses of different types has been

determined[119] from measurements of spin–spin relaxation. Assuming that the bound water is distributed in a monomolecular layer, the authors[119] estimated the surface area of the specimens, the results agreeing satisfactorily with data obtained by other methods.

The relaxation analysis of ^1H NMR data for water adsorbed by lyophilized methaemoglobin crystals[120] showed that 1 g of the protein binds 16 mg of water. For a high moisture content in the compositions (up to 350 mg per g of the polymer) at −40°C a water phase is observed with correlation times intermediate between the values of τ_c for bound and ordinary liquid water.

However, despite the successful application of the NMR method to the determination of the number of bound water molecules by polymers and to the investigation of certain characteristics of their motion, it has been shown[121] for the relaxation of PAA in D_2O and H_2O that the difference between the rates of relaxation of the water associated by the polymer and unassociated water is small and yields no information about the behaviour of hydrated water molecules.

2. The "Freezing" of Adsorbed Water

A reduction of the temperature of the adsorbed mixture below 0°C does not lead to the appearance of breaks on the curves for the temperature variation of T_1 and T_2.[111] The signal amplitude is also constant and indicates a fairly high mobility of the adsorbed water molecules. On the other hand, the T_2–temperature plots for cotton cellulose show an inflexion in the region of 0°C. It has been suggested[111] that a certain amount of water on cotton cellulose behaves analogously to bulk-phase water. Below 243 K, the "freezing" of adsorbed water is observed in both systems and the NMR signal amplitude falls almost to zero at 223 K. The "freezing" process observed at low temperatures is not an indication of the formation of the ice lattice. A similar conclusion was arrived at[115] in a study of the relaxation times of keratin hydrates containing between 12 and 34 wt.% of water and in a study[122] of the relaxation of the water adsorbed in an amount of 33% by the walls of *Bacillus megaterium*.

It has also been discovered[115] that the correlation times of the water molecules adsorbed on keratin are approximately 10^3 times shorter at 270 K than in ice and that in the temperature range 273–240 K the above time is smaller by a factor of 100 than in the bulk-phase water. The authors believe[115] that the ice lattice is formed at high concentrations because some of the water molecules have "moved away" somewhat from the polymer surface and interact only slightly with the latter.

At high water concentrations, for example, in highly hydrated collagen containing more than 0.8 g of D_2O per g of the polymer, it was found that approximately 0.2 g of water is frozen at 0°C.[118]

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The data presented show that the NMR method leads to extensive possibilities for the investigation of polymer–low-molecular-weight substance systems. These possibilities can be greatly expanded by employing ^{13}C NMR spectra and relaxation properties. The application of NMR to the study of such systems is based on the fact that the method makes it possible to assess the molecular mobility, which depends on the concentration of the components, their interaction, the phase state of the specimens, and other factors which determine the macroparameters of the system.

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The Solvation of Mercury Ions and the Formation of Their Complexes in Water and Non-aqueous Solvents

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The characteristic features of the formation of mercury complexes in water and non-aqueous solvents are examined. A relation is established between the stability of the complexes and mercury solvates, on the one hand, and the properties of the solvents, on the other. pHg^{2+} mercury complex stability scales have been constructed on the basis of the concept of ionic activities and the possibility of predicting the activities of complex species, the disproportionation constants, and the solubility products of sparingly soluble mercury salts in non-aqueous media has been demonstrated. Correlations for a series of mercury complexes and solvato-complexes and the prospects for the employment of the quantitative characteristics of solvation in the chemistry of mercury complexes are discussed.
The bibliography includes 180 references.

CONTENTS

I. Introduction 418
II. The structure and properties of mercury atoms and ions 418
III. Characteristic features of the formation of mercury(II) complexes in water 421
IV. Mercury complexes in mixed and non-aqueous solvents 423

I. INTRODUCTION

There has been a considerable growth in recent years of the use of non-aqueous solvents as media for a wide variety of synthesis and analytical determinations. Non-aqueous solvents are being used in increasing amounts in industrial chemistry, which necessitates the study of non-aqueous systems. Investigation of the interaction of dissolved substances with the solvent, the most important of which is solvation, is of considerable interest. The determination of the thermodynamic characteristics of solvation makes it possible to predict properties of electrolytes in non-aqueous media (solubility, acidity, stability of complexes, standard potentials, etc.); the knowledge of the solvation characteristics permits a well-founded choice of solvents in the development of rational methods for non-aqueous titrimetry.

The development of the analytical chemistry of non-aqueous solutions follows a path designed to find stable and selective reagents, among which non-aqueous solutions of heavy metal salts, particularly those of mercury, are being used on an increasing scale. The reactions involving the formation of complex and sparingly soluble mercury compounds are widely employed in electrochemistry, analytical chemistry, and chemical engineering.

This review deals with the literature data for the stabilities of mercury complexes in aqueous and non-aqueous solutions published from 1940 until May, 1976: studies dealing with the chemistry of mixed mercury complexes and organomercury compounds are not considered in the review.

The study of the characteristic features of the solvation of mercury ions and the formation of their complexes makes it possible to discover which atoms and groups shows the greatest tendency towards a donor–acceptor interaction with mercury, to establish the nature of the influence of the solvents on the stability of mercury complexes and the solubility of sparingly soluble mercury compounds, and to estimate the degree of solvation of mercury complexes in order to predict their activities in reactions with organic compounds.

II. THE STRUCTURE AND PROPERTIES OF MERCURY ATOMS AND IONS

1. The Electronic Configuration of Mercury and Its Stable Compounds

The outer $6s$ sublevel of the mercury atom contains two electrons; this sublevel is preceded by the filled $5d$ sublevel and the $5f$ sublevel is unfilled. The Hg^{2+} ion is excited as a result of the transfer of one of the $6s$ electrons either to the $5f$ state or the $6p$ state; energetically the $6s^2 \rightarrow 6sp$ excitation is apparently more favourable. The state of the sp valence electrons determines the structure of mercury compounds [1].

It has been suggested that, in the low-temperature radiolysis [2] and low-temperature electrochemical oxidation [3] of mercury compounds, an unstable mercury(III) ion is produced.

Mercury(I) has formally a non-bonding $d^{10}s^1$ configuration, but in reality exists in the form of the dimer Hg_2^{2+}; one of the electrons in the $6s$ orbital is used to form a covalent Hg–Hg bond and the other is used for ionisation. The polyatomic cations Hg_n^{2+} ($n = 3-6$) have been obtained in reactions in melts and in liquid sulphur dioxide [4].

The Hg_2^{2+} ions exhibit a distinct tendency towards the formation of sparingly soluble compounds. The best known are mercury (I) halides; the fluoride hydrolyses in water, while the remaining mercury(I) halides are sparingly soluble. Mercury(I) perchlorate, sulphate, chlorate, bromate, and iodate are moderately soluble. The soluble mercury(I) salts are associated: their stability constants are as follows: $20(Hg_2SO_4)$; $250[Hg_2(SO_4)_2^{2-}]$; $0.9(Hg_2ClO_4^+)$ (Infeld and Sillén [5]); $1.05[Hg_2(NO_3)_2]$; $0.5(Hg_2NO_3^+)$ (Corbett [6]).

The small amount of data concerning mercury(I) complexes is associated with the weak tendency of Hg_2^{2+} towards the formation of coordinate bonds and with its disproportionation; the latter process takes place particularly vigorously in the presence of ligands forming stable mercury(II) complexes. Mercury(I) complexes can be obtained by introducing into the solution ligands which react to form

ionic bonds: oxalate, succinate, pyrophosphate, and triphosphate[7]. Aniline[8], phenanthroline[9], trifluorophosphine[10], diacetohydrazide[11], and triethanolamine[12] complexes of mercury(I) are known. The dimeric structure of mercury(I) persists in its complexes with arenes; in complexes with *m*-dinitrobenzene a bidentate coordination of NO_2 groups to Hg_2^{2+} was observed[13]. Mercury(I) complexes have one and more, rarely two, ligand molecules[10,14]. Only a few of the complexes—$Hg_2[Ph_3PO]_4(ClO_4)_2$ and $Hg_2[PhNO]_4(ClO_4)_2$—contain four ligand molecules[15].

The highly dissociated mercury(II) salts (perchlorate, nitrate, and sulphate) exhibit ionic properties; the association constants of $Hg(NO_3)_2.0.5H_2O$ are 1.28 (K_1) and 1.0 (K_2).[5] In contrast to the fluorides, the Hg–Hal bond in other halides is covalent. Like the halides, mercury(II) cyanide, oxalate, acetate, thiocyanate, and phosphate are partly or completely dissociated in water. Mercury(II) ions form a considerable number of complex compounds whose stability is characterised below.

The Stability of Aquo- and Solvato-Complexes of Mercury

Mercury ions exist in aqueous solutions in the form of diaquo-ions having the linear structure $Hg(H_2O)_2^{2+}$. The diaquo-complexes can be converted into coordination-saturated tetra-aquo- or even hexa-aquo ions[16]. The thermodynamic functions for the formation of hydrated mercury ions[17,18] are listed below:

	ΔG^0, kcal mole^{-1}	ΔH^0, kcal mole^{-1}	ΔS^0, e.u. (298 K)
Hg^{2+} (aq)	39.365 ± 0.025	40.67 ± 0.050	−8.66 ± 0.20
Hg_2^{2+} (aq)	36.713 ± 0.025	39.87 ± 0.050	15.72 ± 0.20

The enthalpy, energy, and entropy of hydration of the mercury(II) ion at infinite dilution are respectively $-\Delta H_h$ = 443 kcal g-ion^{-1}, $-\Delta G_h$ = 431 kcal g-ion^{-1}, and $-\Delta S_h$ = 40.9 e.u.[19]

The formation of aquo-complexes is complicated by the fact that the metal ion interacts vigorously with one of the ionic forms of the solvent. Mercury(II) hydroxide is an extremely weak base ($K_{diss} = 1.8 \times 10^{-22}$),[20] which exhibits amphoteric properties; this explains the appreciable influence of pH on the state of mercury salts in solution[21]. Thus mercury(II) chloride exists in solution as $HgCl_2$ at pH < 3, undergoes partial hydrolysis at pH 5–7, and at pH > 7 the entire mercury in solution is present as $Hg(OH)_2$.[22] The successive dissociation of hydrate complexes treated as diaquo-acids is characterised by the following negative logarithms of the equilibrium constants for mercury(II): $pk_1 = 2.8$ and $pk_2 = 3.5$;[23,24] for the diaquo-complex of mercury(I), $pk_1 = 4.0$–4.6.[25] The hydrolytic cleavage of mercury salts takes place in any proton-donating solvent; for mercury(II) perchlorate, the corresponding reactions

$$Hg^{2+} + H_2O \overset{k_1}{\rightarrow} HgOH^+ + H^+$$

$$Hg^{2+} + 2H_2O \overset{k_2}{\rightarrow} Hg(OH)_2 + 2H^+$$

are characterised by the constants $pk_1 = 3.70$ and $pk_2 = 6.30$.[26]

The formation of solvato-complexes of mercury is associated with the solvation of all the species involved in the reaction. Solvents (Solv) with appreciable electron-donating properties behave as competing ligands in relation to water[27] and are capable of displacing it from the inner coordination sphere of mercury aquo-ions:

$$[Hg_n(H_2O)_m]^{2+} + l\,Solv \rightleftarrows [Hg_n(Solv)_l(H_2O)_{m-l}]^{2+} + l\,H_2O\,.$$

This process can proceed up to the formation of solvato-complexes having the limiting coordination $[Hg_n(Solv)_m]^{2+}$. A comparative estimate of the stability of solvato-complexes can be made by employing the activity coefficients for the transfer of the corresponding ions; this quantity, designated by[28] $\gamma_t(M^{Z+})$ in accordance with an IUPAC recommendation, characterises the free energy ΔG of the transfer of the M^{Z+} ion from the standard solvent (usually an aqueous solution with unit activity of M^{Z+}) to the test solvent Solv:

$$-\Delta G = RT(\ln K_{[M(Solv)_m]^{z+}} - \ln K_{[M(H_2O)_m]^{z+}}) =$$

$$= zF({}^{H_2O}E^0_{M^{z+}/M} - {}^{Solv}E^0_{M^{z+}/M}) = RT \ln \gamma_t(M^{z+}).$$

Table 1. The negative logarithms of the activity coefficients for the transfer of mercury(I) and mercury(II) ions from water to non-aqueous solvents (25°C).

Solvent	$p\gamma_t(Hg_n^{2+})$		Conditions of measurements		Method	Refs.
	Hg^{2+}	Hg_2^{2+}	Reference electrodes*	Ionic strength		
Methanol (MeOH)	1.7	2.1	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
	3.6	3.8	n.h.e.(H_2O)	0 **	potent.	31
	3.7	3.9		0	spectr.	31
Ethanol (EtOH)	2.8	3.1	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
	4.3	4.6	n.h.e.(H_2O)	0 *	potent.	30
	4.2	4.3	—	0	spectr.	31
Propanol (PrOH)	3.1	4.8	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
	4.8	5.0	n.h.e.(H_2O	0 **	potent.	30
	4.6	5.1	—	0	spectr.	31
Butanol (BuOH)	5.2	5.4	n.h.e.(H_2O)	0 **	potent.	30
	5.2	5.3	—	0	spectr.	31
Pentanol (AmOH)	5.9	6.3	n.h.e.(H_2O)	0 **	potent.	30
	5.4	6.5	—	0	spectr.	31
Hexanol (HexOH)	5.4	5.8	—	0	spectr.	31
Heptanol (HeptOH)	5.5	6.0	—	0	spectr.	31
Ethylene glycol (EG)	−6.8	−5.6	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	32
	−6.9	−3.5	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Propylene carbonate (PC)	—	3.4	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	33
	2.8	1.0	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Acetonitrile (AN)	4.0	3.4	n.h.e.(H_2O)	0.1 (Et_4NClO_4)	potent.	34
	9.0	8.4	n.h.e.(H_2O)	0.1 (Et_4NClO_4)	potent.	35
	3.1	9.0	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Dimethyl sulphoxide (DMSO)	−13.9	−15.2	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	36
	−11.8	−8.6	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Dimethylformamide (DMF)	−12.4	−11.0	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	37–39
	−10.3	−7.6	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Dimethylacetamide (DMA)	−12.4	−11.0	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	39
Hydrazine (Hy)	—	−7.1	Rb+/Rb	0.1 (Et_4NClO_4)	potent.	40
Pyridine (P)	−24.8	—	Fc+/Fc	0.2 ($LiClO_4$)	potent.	41
Pyrrolidone (Pn)	−14.4	−11.8	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	42
N-Methylpyrrolidone (N-MP)	−14.7	−12.5	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	43
N-Methylacetamide (N-MA) (30°C)	−9.2	—	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	44
Acetone (Ac)	1.4	1.0	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Nitromethane (NM)	—	8.5	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	45
	4.5	6.9	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29
Acetic acid (AcOH)	—	−5.2	Fc+/Fc	0.1 (Et_4NClO_4)	polarog.	46
	3.8	5.2	Fc+/Fc	1.0 ($LiClO_4$)	polarog.	29

*Notation: n.h.e. = normal hydrogen electrode; Fc^+/Fc = ferrocene/ferrocenium electrode; Rb^+/Rb = rubidium reference electrode.

** Extrapolation to infinite dilution.

Here $K_{[M(Solv)_m]^{Z+}}$ and $K_{[M(H_2O)_m]^{Z+}}$ are the stability constants of the solvato- and aquo-complexes of the ion M^{Z+} respectively, ${}^{H_2O}E^0_{M^{Z+}/M}$ and ${}^{Solv}E^0_{M^{Z+}/M}$ are the standard potentials of the M^{Z+}/M system in water and the non-aqueous solvent Solv respectively, and F is the Faraday. Thus the quantity $RT \ln \gamma_t(M^{Z+})$ represents the difference between the standard chemical potentials of the ion M^{Z+} in two different solvents.

The activity coefficients for the transfer of mercury(I) and mercury(II) ions from water to non-aqueous solvents of different types have been found[29–46] from electrochemical

and spectroscopic measurements and are listed in Table 1; the polarographic measurements have been carried out using a Strehlow ferrocene/ferrocenium reference electrode[47], the potentiometric measurements were carried out using hydrogen and rubidium reference electrodes, and spectrophotometric measurements were performed using calculations by the Asmus method. The donor–acceptor properties of solvents in relation to a particular ion are characterised by the stability of the corresponding solvato-complexes; such data for mercury(II) solvato-complexes[31] are presented in Table 2.

Table 2. The stabilities of mercury solvato-complexes with organic solvents at 25°C (according to ultra-violet spectroscopic data)[31].

Mercury salt	$\lg K_{st}$ in different solvents*									
	H_2O	MeOH	EtOH	PrOH	BuOH	AmOH	GsOH	GpOH	AcOH	AH
$Hg(ClO_4)_2$	2.6	−1.09	−1.61	−2.01	−2.59	−2.77	−2.80	−2.85	−1.71	−2.01
$Hg_2(NO_3)_2$	—	−0.75	−1.10	−1.29	—	—	—	—	−1.88	−0.48

*The designations of the solvents are the same as in Table 1.

In alcohols the solvation energy of mercury ions decreases compared with water; aliphatic monohydric alcohols are weak electron donors in relation to Pearson's "soft" acids[48]. Thus ΔG for the transfer of $HgCl_2$ from water to ethanol is −1.623 kcal mole^{-1} [49] according to solubility data[49].

Acetonitrile, nitromethane (and probably also sulpholane) constitutes a group of solvents whose dielectric constants and solvating capacities are high, while their electron-donating forces in relation to cations are weak (in the absence of specific interactions). In consequence of the weaker solvation of mercury ions, the mercurimetric oxidation of dihydroxybenzenes[50] and inorganic cations[51] as well as electrophilic addition of mercury(II) salts to unsaturated hydrocarbons[52–54] proceed faster in alcohols and acetic and trifluoroacetic acids. The specific interaction of mercury ions with dipolar aprotic solvents leads to the formation of stable solvato-complexes of mercury(I) and mercury(II) with dimethyl sulphoxide, dimethylformamide, dimethylacetamide, pyrrolidinone, and *N*-methylpyrrolidinone. The complexes with dimethyl sulphoxide are particularly stable: the solvent molecules have two electron-donating centres. The formula $3HgCl_2.2Solv$, with coordination via oxygen, has been attributed[55] to mercury(II) chloride complexes with sulphoxides. There is a possibility[56] of the coordination of mercury(II) nitrate to acetonitrile; the coordination number was found to be 3.5.[57] The hydrolysis of acetonitrile under the influence of traces of water in a solvent, catalysed by mercury(II) salts, proceeds with formation of acetamide complexes of mercury; in contrast to transition metal complexes, the latter involve coordination via the nitrogen atom[58,59].

The polarographic data presented in Table 1 were obtained on the hypothesis that $E_{1/2} \simeq E^0$; although the formal electrode potentials, measured in the presence of supporting electrolytes, do not reflect directly the changes in the free energy of formation of ions, they nevertheless give an idea about the solvating capacity of solvents. (Comparison of the half-wave potentials and the activity coefficients calculated with their aid is justified when the measurements are performed in identical supporting electrolyte solutions and when the same working hypothesis is used.)

Table 3. The electrode potentials of the Hg^{2+}–Hg_2^{2+}–Hg^0 system (at 25°C)*.

Solvent	Process potential, V			Conditions of measurements		Refs.
	$Hg^{2+}\rightarrow Hg_2^{2+}$	$Hg_2^{2+}\rightarrow Hg^0$	$Hg^{2+}\rightarrow Hg^0$	Reference electrode	Ionic strength	
H_2O	0.907	0.792	0.850	n.h.e.(H_2O)	0	62,63
H_2O	—	—	2.48	Rb^+/Rb	0	60
H_2O	—	0.390	0.450	Fc^+/Fc	0.1 (Et_4NClO_4)	64
H_2O	—	0.430	0.460	Fc^+/Fc	1.0 ($LiClO_4$)	65,66
MeOH	—	0.764	—	n.h.e.(H_2O)	0	67
MeOH	—	0.490	0.510	Fc^+/Fc	1.0 ($LiClO_4$)	65
MeOH	—	0.740	—	n.h.e.(MeOH)	0	68
EtOH	—	0.760	0.739	n.h.e.(EtOH)	0	69
EtOH	—	0.520	0.540	Fc^+/Fc	1.0 ($LiClO_4$)	65
EG	—	0.220	0.245	Fc^+/Fc	0.1 (Et_4NClO_4)	64
EG		0.330	0.240	Fc^+/Fc	1.0 ($LiClO_4$)	65
Pn	—	0.035	0.015	Fc^+/Fc	0.1 (Et_4NClO_4)	70
N-MP	0.021	0.029	0.025	Fc^+/Fc	0.1 ($LiClO_4$)	43,71
Hy	—	0.770	—	Fc^+/Fc	0	28
Hy	—	2.880	—	n.h.e.(Hy)	0	73
DMF	—	0.079	0.090	Hg/Hg_x^{2+}	0.1 (Et_4NClO_4)	38
DMF	—	0.160	0.210	Fc^+/Fc	1.0 ($LiClO_4$)	65
DMF	0.100	0.058	—	Fc^+/Fc	0.1 (Et_4NClO_4)	74,75
DMF	—	—	0.90	BBCr (I)	0.1 (Et_4NClO_4)	76
DMA	0.110	0.070	0.090	Fc^+/Fc	0.1 (Et_4NClO_4)	71
PN	—	—	2.56	Rb^+/Rb	0.1 (Et_4NClO_4)	60
BN	—	—	2.58	Rb^+/Rb	0.1 (Et_4NClO_4)	60
BN	1.45	1.25	—	BBCr (I)	0.1 (Et_4NClO_4)	76
iso-BN	—	—	2.55	Rb^+/Rb	0.1 (Et_4NClO_4)	60
AN	—	0.482	0.490	Fc^+/Fc	0.1 ($LiClO_4$)	77
AN	—	—	0.993	n.h.e.(H_2O)	0	68
AN	—	0.250	—	n.h.e.(AN)	0	68
AN	0.7	0.5	—	sat.c.e.	0.1 ($NaNO_3$)	78
AN	—	0.690	0.550	Fc^+/Fc	1.0 ($LiClO_4$)	65
AN	—	—	2.58	Rb^+/Rb	0.1 (Et_4NClO_4)	60
AN	1.4	1.2	—	BBCr (I)	0.1 (Et_4NClO_4)	76
PC	0.150	0.495	—	Fc^+/Fc	0.1 (Et_4NClO_4)	79
PC	—	0.460	0.540	Fc^+/Fc	1.0 ($LiClO_4$)	65
PC	—	—	1.33	BBCr (I)	0.1 (Et_4NClO_4)	76
DMSO	0.882	0.684	0.783	n.h.e.(DMSO)	0.1 (Et_4NClO_4)	80
DMSO	—	—	0.80	BBCr (I)	0.1 (Et_4NClO_4)	76
DMSO	—	0.17	0.12	Fc^+/Fc	1.0 ($LiClO_4$)	65
Ac	—	0.716	—	n.h.e.(H_2O)	0	67
Ac	—	—	2.65	Rb^+/Rb	0.1 (Et_4NClO_4)	76
Ac	—	0.46	0.50	Fc^+/Fc	1.0 ($LiClO_4$)	65
NM	—	0.640	—	Fc^+/Fc	0.1 (Et_4NClO_4)	45
NM	—	0.63	0.59	Fc^+/Fc	1.0 ($LiClO_4$)	65
NB	—	—	0.14	BBCr (I)	0.1 (Et_4NClO_4)	76
HCOOH	—	0.180	—	n.h.e.(HCOOH)	0	68
AcOH	—	0.240	—	Fc^+/Fc	0.1 (Et_4NClO_4)	46
AcOH	—	0.58	0.57	Fc^+/Fc	1.0 ($LiClO)_4$	65
P	—	—	0.180	$Ag/AgClO_4$	0.2 ($LiClO_4$)	41
P-H_2O						
10 wt.% P	—	0.230	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
20 wt.% P	—	0.227	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
40 wt.% P	—	0.249	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
60 wt.% P	—	0.264	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
80 wt.% P	—	0.264	—	Fc^+/Fc	0.5 ($LiClO_4$)	81
EtOH-H_2O 10 wt.% EtOH	0.591	—	—	n.h.e.(EtOH)	0	69
70 wt.% EtOH	0.723	—	—	n.h.e.(EtOH)	0	69

*Notation: PN = propionitrile; BN = butyronitrile; iso-BN = isobutyronitrile; NB = nitrobenzene; BBCr(I) = bisbiphenylchromium(I) iodide reference electrode.

According to the anodic dissolution potentials for mercury[60], the solvation energy of mercury(I) ions and the stability of mercury(I) perchlorate in water are higher than in acetone or acetonitrile; in aromatic nitriles the solvation energy of mercury ions is greatly reduced compared with water. The decrease of the solvating capacity of solvents in relation to mercury ions proceeds in the

following sequence: dimethyl sulphoxide > *N*-methylpyrrolidinone > pyrrolidinone > dimethylformamide, dimethylacetamide > ethylene glycol > water > acetone > methanol > ethanol > propylene carbonate > propanol > acetic acid > nitromethane > acetonitrile.

3. Disproportionation and Standard Potentials of Mercury Systems

The energies of the mercury(I) disproportionation reactions are low; thus $\Delta H = 8$ kcal mole^{-1} and $\Delta G = 6.3$ kcal mole^{-1} for the reaction[81]

$$Hg_2Cl_2 \rightleftarrows HgCl_2 + Hg \cdot$$

It is possible to determine K_d indirectly via the standard potentials:

$$pK_d = \frac{E^0_{Hg^{2+}/Hg^0} - E^0_{Hg_2^{2+}/Hg^0}}{2.3RT/zF}, \quad (1)$$

where z is the number of electrons. The literature data for the standard and half-wave potentials of mercury systems are presented in Table 3 and the values of pK_d calculated by Eqn. (1) are in Table 4.

Table 4. The negative logarithms of the disproportionation constants of mercury(I) ions calculated from the values of E° on the ferrocene scale.

Solvent	pK_d	References	Solvent	pK_d	References
H_2O	2.07	62	PC	2.76	65
H_2O	2.22	63	DMF	0.70±0.25	74
H_2O	1.14	65	DMF	−1.38	65
MeOH	0.69	65	DMA	0.60±0.25	39
EtOH	0.69	65	NM	−1.38	65
PrOH	−1.03	65	Ac	1.38	65
EG	−3.10	65	AcOH	−0.35	65
EG	0.85±0.25	72	DMSO	3.4	80
Pn	−0.69	42	DMSO	1.6	82
N-MP	−0.14±0.09	71	DMSO	−1.71	65
N-MP	−0.1±0.1	70	AN	2.7±2	77

Although comparison of the potentials measured on different scales is in fact difficult, it is nevertheless evident that the potentials of the mercury systems are more negative in dimethyl sulphoxide, dimethylformamide, dimethylacetamide, *N*-methylpyrrolidinone, and ethylene glycol than in water. The literature data[46] for acetic acid are probably erroneous; this solvent causes only slight solvation of inorganic cations[28]. Acetonitrile, propylene carbonate, and nitromethane weakly solvate mercury ions; in these solvents the oxidising properties of mercury ions should be manifested to a greater extent.

The values of K_d (Table 4) have been determined in many instances with a considerable error; nevertheless one can note that Hg_2^{2+} ions are stable in water (disproportionation takes place to the extent of 1%), propylene carbonate, and an acetic anhydride–acetic acid mixture (disproportionation to the extent of 5%).[83] The disproportionation of Hg_2^{2+} takes place partly in *N*-methylpyrrolidinone, dimethylformamide, and dimethylacetamide and almost wholly in ethanolamine[84], ethylenediamine, and *N*-methylacetamide[86].

Any significant weakening of the Hg–Hg bond promotes the disproportionation reaction; reagents which decrease the activity of Hg^{2+} as a result of the formation of complex or sparingly soluble mercury(II) compounds favour disproportionation.

It is to be expected that the solvation of both valence forms contributes to the change in the disproportionation constants; indeed, since

$$K_d = a_{Hg^{2+}}/a_{Hg_2^{2+}}$$

$$\text{and } K_d^{Solv} = K_d^{H_2O} \frac{\gamma_t(Hg^{2+})}{\gamma_t(Hg_2^{2+})},$$

one can write

$$pK_d^{Solv} = pK_d^{H_2O} + p\gamma_t(Hg^{2+}) - p\gamma_t(Hg_2^{2+}).$$

In a real process disproportionation of a sparingly soluble mercury(I) salt (in electrodes of the second kind, for example) is associated with the stability of the complexes formed in the reaction; for the reaction

$$Hg_2L_2 + mL^- \overset{K'_d}{\rightleftarrows} [HgL_{m+2}]^{m-} + Hg, \quad (2)$$

the negative logarithm of the disproportionation constant is

$$pK'_d = pK_d + pSP_{Hg_2L_2} + pK_{[HgL_{m+2}]^{m-}},$$

where $SP_{Hg_2L_2}$ is the solubility product of the salt undergoing disproportionation.

The change in the values of pK'_d on passing from water to the non-aqueous solvent Solv is associated with the nature of the solvation of all the compounds involved in equilibrium (2):

$$(pK'_d)^{Solv} = (pK'_d)^{H_2O} + p\gamma_t([HgL_{m+2}]^{m-}) - m \cdot p\gamma_t(L^-). \quad (3)$$

III. CHARACTERISTIC FEATURES OF THE FORMATION OF MERCURY(II) COMPLEXES IN WATER

1. The Electronic Structure of Mercury Complexes

The characteristic coordination numbers n of mercury(II) are 2 and 4; however, complexes with $n = 5$ are known[87]. The formation of octahedral complexes[88] is less typical; for example, hexa-aquo-complexes of mercury perchlorate are formed in water only at low salt concentrations[89]; an increase of the concentration leads to the formation of tetra-aquo-complexes.

Donor–acceptor complexes of mercury are formed as a result of the supply by the ligand electron-donor atom of a lone electron pair to an acceptor s or p orbital of mercury(II). The donor electrons fill the unoccupied s and p sublevels of the external level and form hybrid sp^3 orbitals; furthermore, the ligand itself can behave as an acceptor in relation to the electrons of the $5d$ sublevel of mercury.

Since the $5d$ sublevel is filled, stabilisation by the ligand field is not characteristic of mercury complexes; the stereochemistry of the complexes is determined exclusively by ion size, electrostatic forces, and the covalence of the bonds. The high stability of the mercury complexes has been explained[90] by the employment of the hybrid sp^3 orbitals of the metal and of the most stable tetrahedral configuration in coordination.

2. The Properties of Ligands and the Stability of Complexes

Mercury(II) is classified[91] as a typical representative of "soft" acids, the sequence of the changes in the stability of the complex species being identified with the sequence in the changes in the metal–ligand bond strength. Mercury ions form stronger complexes with the majority of ligands than other *d* elements; this applies to both acido-complexes and to ammines and complexonates. The stability of the complexes is determined to some extent by the nature of the polarisation of the ligands; the increase of the polarisability of the ligands in the series $Cl^- < Br^- < I^-$ (decrease of electron affinity[92]) is combined with an increase in the same sequence of the tendency of the ligands towards the formation of π bonds and with increase in stability of the complexes[62]. This sequence of the changes in the stability of mercury halide complexes indicates an appreciable role of the enthalpy component in complex formation[93].

A remarkable feature of the stereochemistry of mercury chloro-complexes is a tendency towards the retention of the linearity of the Cl–Hg–Cl group. The free energy of formation ΔG (kcal mole^{-1}) of hydrated complex ions varies as follows for halide[94-98] and cyanide[97,99] complexes: 22.1($HgCl_4^{2-}$); 29.5($HgBr_4^{2-}$); 41.3(HgI_4^{2-}); 54.8[$Hg(CN)_4^{2-}$]. The increased stability of the mercury cyanide complex is accounted for by the greater strength of the Hg–CN bond compared with Hg–Hal.[97]

The increase in the stability of the complexes is associated with the formation of a donor π bond[100]; correspondingly, complexes with electron-donating sulphur, selenium, and phosphorus atoms [$S{=}C(NH_2)_2$, $Se{=}C(NH_2)_2$, $HO(CH_2)_2$–S–$(CH_2)_2$–NH_2, Ph_2–$PC_6H_4SO_3^-$, and $HO(CH_2)_2PEt_2$] are extremely stable[101,102]. This also applies to mercury sulphide[103], thiocyanate[104], and selenocyanate[105] complexes.

A relatively low stability is characteristic of mercury complexes with "hard" ligands (Hal^-, NR_3, NH_3, N_3^-, OH^-, SO_4^{2-}, NO_2^-, NO_3^-, and $RCOO^-$); the formation of a donor–acceptor σ bond predominates in this case[101,106-108].

A decrease of the strength of the Hg–L bond in the series Se > S > N > O is characteristic of atoms with filled *d* orbitals, which are capable of forming $d_\pi - d_\pi$ bonds with atoms having vacant *d* orbitals[90]. The stability of amino-complexes exceeds that of carboxylate complexes approximately by 10 orders of magnitude; the Hg–N bond is 2–2.5 times stronger than the Hg–O and Hg–C bonds (the free energy of the latter is 24–36 kcal mole^{-1} [109]).

Mercury complexes with carboxylic acids[110-118] and hydroxyacids[113-115] usually have the 1:1 (rarely 1:2) composition and are characterised by a certain stability ($\lg K_{st} \leq 8$). The replacement of an oxygen atom in the ligand molecule by sulphur entails a sharp increase in the stability of the complexes, which is characteristic of thiocarboxylates[119-122] and unithiol derivatives[123,124].

The basicity of the nitrogen atom and the stability of complexes. The stability of the donor–acceptor bond between nitrogen and mercury atoms is determined by the density of the electron cloud at the nitrogen atom. The stability of mercury complexes with nitrogen-containing ligands is higher the greater the basicity of the ligands; this relation is maintained for ligands of different types[125-127] and can be represented by the following equations:

$$\lg K_{HgL} = 1.08\, p K_{HL} - 0.53 \text{ (ammines)};$$

$$\lg K_{HgL} = 0.91\, p K_{HL} + 1.81 \text{ (barbiturates)};$$

$$\lg K_{HgL} = 1.25\, p K_{HL} + 1.48 \text{ (sulphamides)};$$

$$\lg K_{HgL} = 0.73\, p K_{HL} + 1.01 \text{ (hydroxypyridines and hydroxypyrimidines)}.$$

Steric hindrance and the presence in ligands of functional groups capable of interacting with mercury(II) cause a deviation of plots of $\lg K_{HgL}$ from linearity. Analogous relations are characteristic also of mercury complexonates. The slope of these lines usually depends[128] on the ionisation potential of the central atom and the polarisation of the ligands by the metal ion. Such relations for aliphatic ammines have slopes close to unity; with intensification of the capacity of the metal ion for the formation of d_π bonds and with increase of the degree of stabilisation in the ligand field, the slopes increase. The linearity of these relations holds only for a series of ligands which are mutually similar structurally, form the same number of chelate rings, and have the same capacity for the formation of π bonds.

Pyrimidine derivatives interact with mercury(II) ions in three possible ways: by the coordination of the carbonyl oxygen of the mercury salt with the neutral ligand; by electrophilic attack with displacement of a proton and the formation of an Hg–C bond; by electrophilic attack with formation of an N–Hg bond[129]. Alkylamines[130-133], π-electron systems (pyridine[132] and aniline[134]), and amino-acids[135-137] bind mercury ions more weakly than other nitrogen-containing ligands (purines and pyrimidines, and imidazole).

Cyclisation and the stability of the complexes. The presence of three five-membered rings in the mercury(II) complex of EDTA is responsible for the highest stability of the complex[138]. Mercury complexes of triethylenediaminetetra-acetic[139], cyclohexane-1,2-diaminetetra-acetic[140], diethylenetriaminepenta-acetic[141], and triethylenetetraminehexa-acetic[142] acids have similar structures. The enhancement of the basic properties of these ligands compared with EDTA stabilises the mercury complexes.

The stability of mercury compounds with complexones having the general formula $(HOOCCH)_2$–$(CH_2)_X$–$(CH_2COOH)_2$ varies non-linearly with increasing x, reaching a minimum for six-membered rings ($x = 3$). A further increase of x leads to the stabilisation of the complexonates: with increase in the size of the ring, its strain, due to the bending of the *sp* orbitals of the mercury ion, diminishes[90].

Complexes with nitrilotriacetate[115], ethylenediaminedimalonic, ethylenediaminedisuccinic, and ethylenediaminediglutaric acids[142], propylenediaminetetra-acetic acid[143], dimethylethylenediaminetetra-acetic acid[140], ethylene disulphide diacetic acid[144] [data for this ligand are not in this reference (Ed. of Translation)], and other complexones[145,146] have low stability constants ($\lg K_{st} \leq 17$). Introduction of sulphur into the complexone molecule leads to a marked stabilisation of phthalyltetrathioacetic acid complexes: $\lg K_{st}[Hg(OH)_2L] = 45$.[147]

Olefin complexes. Many olefin reactions proceed via the formation of intermediate compounds of olefins with mercury atoms; the highest strength of the mercury–olefin bond is due to the involvement of both σ-donor and π-acceptor orbitals in complex formation. The activation of olefins by complexes of mercury and other metals[148] leads to the loosening and a decrease of the multiplicity of

the C=C bond and also to an increase of the positive charge on the carbon atoms owing to the formation of a three-membered ring in which the metal ion plays the role of a heteroatom. The stability constants of the ethylene, propene, and cyclohexene complexes of mercury are [149,150] respectively 1.4×10^4, 1.9×10^4, and 2.2×10^4.

IV. MERCURY COMPLEXES IN MIXED AND NON-AQUEOUS SOLVENTS

1. The Properties of the Solvents and the Stability of the Complexes

The formation of mercury complexes in non-aqueous solvents is determined by the nature of the solvation of mercury ions and the ligands: the stability of the complex species $[HgL_n]^{(2-nl)+}$ is greater than that of the solvato-complexes $[Hg(Solv)_m]^{2+}$ and $[L(Solv)_p]^{l-}$, and the ligands L^{l-} displace solvent molecules more or less readily from the inner coordination sphere of the solvato-complex of mercury:

$$[Hg(Solv)_m]^{2+} + n[L(Solv)_p]^{l-} \rightleftarrows [HgL_n]^{(2-nl)+} + (m + np)\,Solv \quad .$$

Otherwise the stability of the complexes $[HgL_n]^{(2-nl)+}$ is low. In the majority of mixed solvents the influence of the organic cosolvent on the stability of the complexes can be accounted for from the electrostatic standpoints described by the Born equation; indeed the relation between $\lg K$ and $1/\epsilon$ is linear for mercury halide, thiocyanate, and cyanide complexes in aqueous pyridine solutions [81], for cyanide complexes in water–ethanolamine and water–ethylenediamine mixtures [86], and for chloride complexes in aqueous methanol [151], ethanolamine, and ethanol [152] mixtures. The absence of such linearity for the *N*-methylacetamide–dimethylformamide system has been explained [44] by the appreciable electron-donating properties of *N*-methylacetamide in relation to mercury(II): the specific interaction of mercury ions with the solvent can make a significant contribution to the change in the stability of the complex when the composition of the medium is altered.

The introduction of donor-active solvents into aqueous solutions weakens hydration and increases the coordination number to $n > 4$. On the other hand, in pure non-aqueous solvents the solvation of ions can reduce their coordination capacity. Thus in aqueous methanol (up to 10 M MeOH) and aqueous ethanol (9 M EtOH) mixtures mercury thiocyanate complexes $[Hg(SCN)_n]^{(2-n)+}$ with $n = 5$ are formed, whereas in aqueous acetone (10M acetone) n is actually 6; [158] in pure ethanol and acetone n usually does not exceed 4. Similarly, in the formation of acetate complexes in water and methanol n does not exceed 3, while in ethanol and ethylene glycol n decreases to 2. [111,112]

The literature data on the stability of mercury complexes in non-aqueous solvents are numerous: they are available for halide and cyanide complexes in methanol [153-155], ethanol [152-154], acetone [153,154], ethylene glycol [156], pyrrolidone [43], *N*-methylpyrrolidone [70,71], dimethylformamide [39,72,154,157-161], dimethylacetamide [39,162], *N*-methylacetamide [44], ethylenediamine [85], ethanolamine [152], pyridine [41], liquid ammonia [163], acetonitrile [35,164-168], and dimethylsulphoxide [79,82,158-160]. The high stability of mono- and di-ethanolamine complexes of mercury in ethanol [152] and the dithizone, thiourea, and thioacetate complexes in dimethylformamide [39,169] has been noted.

The appreciable solvation of heavy metal ions in aprotic dipolar solvents [28,170] should have entailed a decrease of the stability of the mercury complexes in these media compared with their stability in water. Assuming that the electron-donating characteristics of dimethylsulphoxide, dimethylformamide, and dimethylacetamide are virtually the same, equal stabilities of the complexes in these solvents would be expected. However, the stability of the complexes is apparently determined not so much by the donor number (although the formation of the complexes is undoubtedly facilitated by a decrease of the donor numbers of the medium [172]) and the dielectric constant as by the solvation energies of the anions (ligands and complex species). The weak solvation of anions in aprotic dipolar solvents [173] leads to an increase of the stability of the coordination iodo-complexes in these media by 1–5 orders of magnitude and of the chloro- and bromo-complexes by 10–15 orders of magnitude compared with the stability of the same species in water. In aqueous solutions the stability of mercury complexes increases in the sequence $HgCl_2 < HgCl_4^{2-} < Hg(SCN)_2$, $HgBr_2 < HgBr_4^{2-} < HgI_2 < HgI_4^{2-}$. This series changes for aprotic dipolar solvents [4]; for example, in dimethyl sulphoxide and dimethylformamide it is $Hg(SCN)_2 < Hg(SCN)_4^{2-} < HgCl_2 < HgBr_2 < HgI_2 < HgCl_4^{2-} < HgBr_4^{2-} < HgI_4^{2-}$.

In alcoholic mercury halide solutions the complexes $HgHal_3^-$ and $HgHal_4^{2-}$ predominate [154,156] (a situation analogous to that in aqueous solutions [174]), but their stability is low: in methanol $K_{st} = (1.10-1.86) \times 10^4$ for HgI_3^-. [152] The presence of only $HgBr_3^-$ with $\lg K_{st} = 3.3$ was noted in acetone [154,175]. The stability of mercury iodide solvato-complexes with alcohols and acetone decreases in the sequence methanol > propanol > butanol > hexanol > acetone [176].

The heats of formation of mercury iodide complexes in amides and sulphoxides are independent of the radius of the outer-sphere cation [159]: the complexes HgI_3^- and HgI_4^{2-} are very stable. The logarithms of their stability constants are respectively 30.4 and 32.6 in dimethyl sulphoxide [80] and 33.3 and 37.3 in dimethylformamide [39]. The formation of mercury halide and thiocyanate complexes in these solvents is accompanied by an exothermic heat change; the heats of formation of complexes having analogous compositions are higher in dimethylformamide than in dimethyl sulphoxide [160]. The complexes are particularly stable in acetonitrile, where the species HgL_3^-, HgL_4^{2-} and $Hg_2L_5^-$ exist [164].

2. The Stability Scales of Mercury Complexes

The interpretation of the measurements and comparison of the stabilities of the complex species in various solvents become possible when the concept of ionic activity is used; the quantities $p\gamma_t(Hg^{2+})$ constitute a basis for the construction of scales characterising the relative affinities of the ligands for Hg^{2+} ions; some of these pHg^{2+} scales are illustrated in Fig. 1. The scales are displaced relative to the stability scale for mercury complexes in water by $p\gamma_t(Hg^{2+})$; [62] the beginning of each scale corresponds to $[Hg(Solv)_m^{2+}] = 1$ M. The greater the downward displacement of the pHg^{2+} scale in a solvent (Solv) the greater the ability of solvent molecules to displace the ligands L^{l-} lying higher in this series from the inner coordination spheres of the complexes. The logarithms of the exchange equilibrium constants correspond to the distance between the corresponding "ligand donor–acceptor" pairs on the

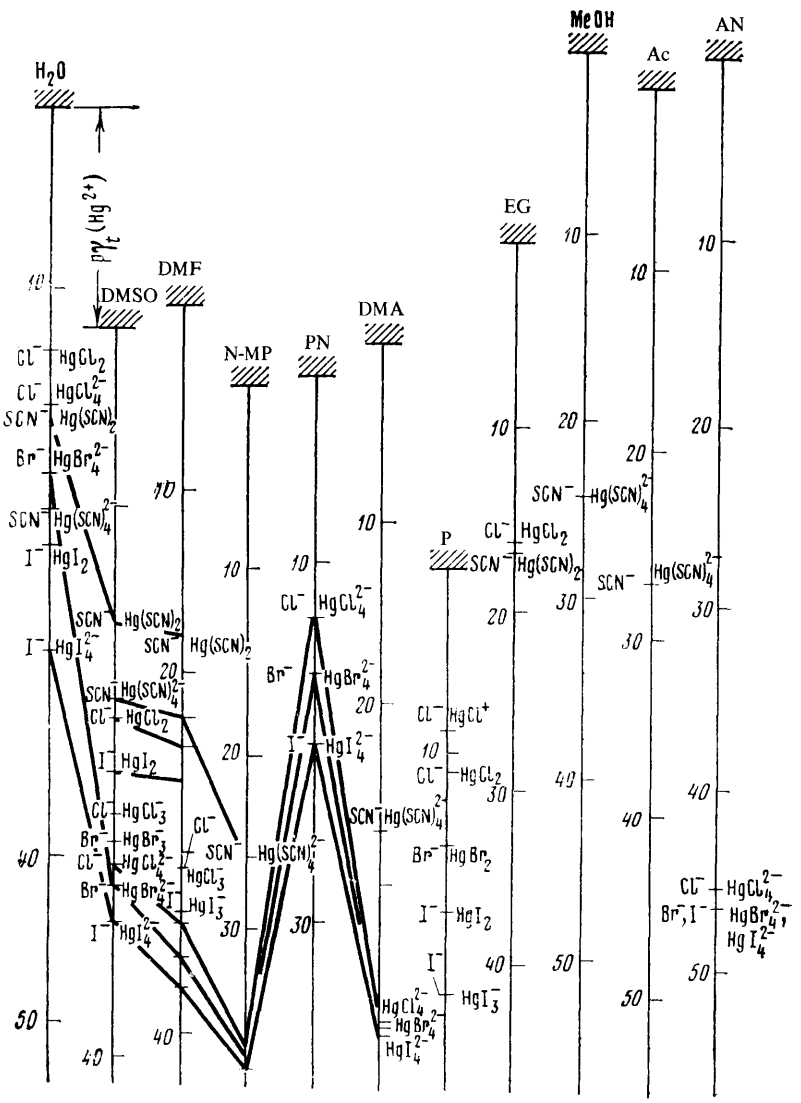


Figure 1. pHg^{2+} stability scales for mercury complexes in water and non-aqueous solvents. The designations of the solvents correspond to those in Table 1.

pHg^{2+} scale in terms of units of $\lg K$. Thus the reaction

$$HgCl_2 + 2SCN^- \overset{K}{\rightleftarrows} Hg(SCN)_2 + 2Cl^-$$

proceeds to the right in water ($\lg K = 3.6$), changes direction in dimethylformamide and dimethyl sulphoxide ($\lg K = -6.4$ and -5.1 respectively), and in *N*-methylpyrrolidone any halide displaces a thiocyanate ion from its mercury complex.

Evidently the removal of traces of water from solvents which weakly solvate Hg^{2+} cations (acetonitrile, nitromethane, and trifluoroacetic acid) is especially important: in aqueous acetonitrile mixtures water molecules occupy sites in the inner coordination sphere of the complex up to appreciable acetonitrile concentrations. On the other hand, the presence of even small amounts of amides in aqueous solutions of mercury compounds causes transolvation of the coordination sphere with replacement of water molecules (partial or complete) by the molecules of the organic cosolvent.

The positions of the complex species $[HgL_n]^{(2-nl)+}$ on the pHg^{2+} scale is determined by the solvation of all the species involved in the complex-formation reaction

$$p K^{Solv}_{[HgL_n]^{(2-nl)+}} = p K^{H_2O}_{[HgL_n]^{(2-nl)+}} + p\gamma_t(Hg^{2+}) + n \cdot p\gamma_t(L^{l-}) - p\gamma_t([HgL_n]^{(2-nl)+}). \quad (4)$$

Eqn. (4) has been used[54] to calculate the activity coefficients of mercury complexes. Aprotic dipolar solvents weakly solvate anionic complexes of mercury: for the chloride complex with the limiting coordination ($n = 4$), the values of $p\gamma_t$ are 8.8 in dimethylformamide, 7.7 in dimethyl sulphoxide, and 10.1 in dimethylacetamide. The weak solvation of cationic and molecular complexes of mercury in hydroxylated solvents leads to an increase of the activity of these complexes in reactions involving electrophilic addition to olefins.

The equation

$$pSP^{Solv}_{Hg_2L_2} = pSP^{H_2O}_{Hg_2L_2} + p\gamma_t(Hg_2^{2+}) + 2p\gamma_t(L^-) \quad (5)$$

for the solubility products of sparingly soluble mercury(I) compounds, which is analogous to Eqn. (4), makes it possible to calculate from the ionic activities and the known values of $SP_{Hg_2L_2}$ in water the solubilities of mercury(I) salts in non-aqueous solvents and to solve with the aid of Eqn. (3) the problem of the disproportionation of mercury halides in reference electrodes in measurements in non-aqueous media. Such calculations have demonstrated the absence of the disproportionation of sparingly soluble mercury(I) salts in the absence of an excess of ligands even in aprotic dipolar solvents. When there is an excess of ligands (which is typical for electrodes of the second kind) mercury halides are resistant to disproportionation in alcohols, formamide, and acetic acids [177].

3. Correlations in the Series of Mercury Complexes and Solvates

The experimental determination of the equilibrium constants for mercury systems in both water and non-aqueous solvents is complicated by solvolysis and disproportionation reactions. It is therefore of interest to follow the possibility of using methods of comparative calculation for predicting the stability of mercury(II) complexes and ionic activity coefficients.

The ratio of the constants for successive coordination stages. The successive equilibrium constants for individual stages involving many metal ion complexes with the same ligands usually decrease, as expected from an examination of statistical factors, steric effects, and Coulombic interaction [90]. According to Bjerrum [23,106], the stability of complexes corresponding to successive coordination stages is determined by the ratio

$$\frac{k_n}{k_{n+1}} = \frac{(N-n+1)(n+1)}{(N-n)\cdot n}, \quad (6)$$

where k_n and k_{n+1} are the stability constants of the nth and $(n+1)$th coordination stages and N is the maximum coordination number of the ion. However Eqn. (6) cannot fully characterise the stability of successively formed mercury(II) complex species: polarisation, statistical, and solvation effects are responsible for deviations of the experimental data from those calculated by the equation [92]

$$\frac{\lg K_n}{n} = \lg k_1 - \lambda(n-1). \quad (7)$$

The deviations are especially large for the second coordination stage in aqueous solutions and reach 1.9 lg K units [54]. This stage is characterised by a high stability of the complexes owing to the change in the structure of complex species in the course of their successive formation. Thus the complex $HgCl^+$ is a distorted tetrahedron with the mercury atom in the centre and the Cl^- ion and the three water molecules at the vertices; $HgCl_2$ is a flattened octahedron with chloride ions (in the *trans*-positions) and four water molecules (at the corners of the square) at the vertices; $HgCl_3^-$ is a distorted tetrahedron with a water molecule at a vertex; finally $HgCl_4^{2-}$ is a regular tetrahedron [178]. The highest exothermic heat change corresponds to the second coordination stage for mercury complexes in water. With increase of n, the degree of outer-sphere hydration of the complexes becomes more pronounced, which, when combined with structural changes, makes the heats of successive complex-formation stages less exothermic [178,179].

The dependence of $\lg K_n/n$ on n for mercury complexes in non-aqueous solvents is linear, which makes it possible to determine the approximate stability constants of the complexes HgL^+ in methanol, dimethylformamide, dimethyl sulphoxide, N-methylacetamide, and ammonia [54].

Relation between the electrochemical and spectroscopic manifestations of solvation. Numerous examples of the parallel variation of the electrochemical and spectroscopic characteristics of compounds have been described in the literature [180]. Indeed the oxidation-reduction potentials are proportional to the energies of the lowest unoccupied and highest occupied molecular orbitals and the long-wavelength absorption frequency in the electronic spectrum is equal to the difference between the energies of the two frontal mercury orbitals. In the series of mercury solvato-complexes there is [30,31,65] a linear correlation between the changes in the standard potential ΔE^0 (the half-wave potential $\Delta E_{1/2}$) and the solvatochromic effect; for protic and aprotic dipolar solvents, these relations are respectively

$$\Delta E^0 = -0.67(\Delta\lambda_{max}) + 6.33, \quad (8)$$

$$\Delta E_{1/2} = -2.20(\Delta\lambda_{max}) - 1.32. \quad (9)$$

The empirical Eqns. (8) and (9) can be used to predict certain spectroscopic properties on the basis of preliminary electrochemical measurements.

Correlations between the activity coefficients and properties of the solvents. The dependence of $\lg\gamma_t(Hg_n^{2+})$ on the reciprocals of the dielectric constant $1/\epsilon$ and the negative logarithms of the autoprotolysis constants pK_S of the solvents is usually non-linear [65]. The scatter of the points indicates an appreciable role of specific solvation: owing to the presence of unfilled 6*s* orbitals in mercury, there is a possibility of a donor–acceptor interaction of its ions with the lone electron pairs of solvent molecules. However, for solvents of the same type (aliphatic monohydric alcohols) distinct linear relations between $p\gamma_t(Hg_n^{2+})$ and $(1/\epsilon)pK_S$ are observed [29]. The dependence of $\lg\gamma_t(Hg_n^{2+})$ on the donor numbers DN of the solvents is linear [29] for $DN > 10$; the non-linearity of the relation in the region of low donor numbers can be attributed to ion association in media with low dielectric constants and low solvating capacity.

Correlation in the series of isoelectronic ions. The linearity of the relations between the enthalpies of complex formation by ions with isoelectronic structures and similar radii [101,106] suggests that the variation of the stabilities of the complexes is also linear. Such relations for mercury(II) and silver(I) ions in water, dimethyl sulphoxide, and dimethylformamide are described [54] by the equations

$$\lg K^{H_2O}_{AgX_2^-} = 0.67\lg K^{H_2O}_{HgX_2} - 4.7,$$

$$\lg K^{DMSO}_{AgX_2^-} = 0.57\lg K^{DMSO}_{HgX_2} - 0.75,$$

$$\lg K^{DMF}_{AgX_2^-} = 0.71\lg K^{DMF}_{HgX_2} - 0.52,$$

which can be used to estimate the stabilities of the molecular complexes of mercury from data for the analogous

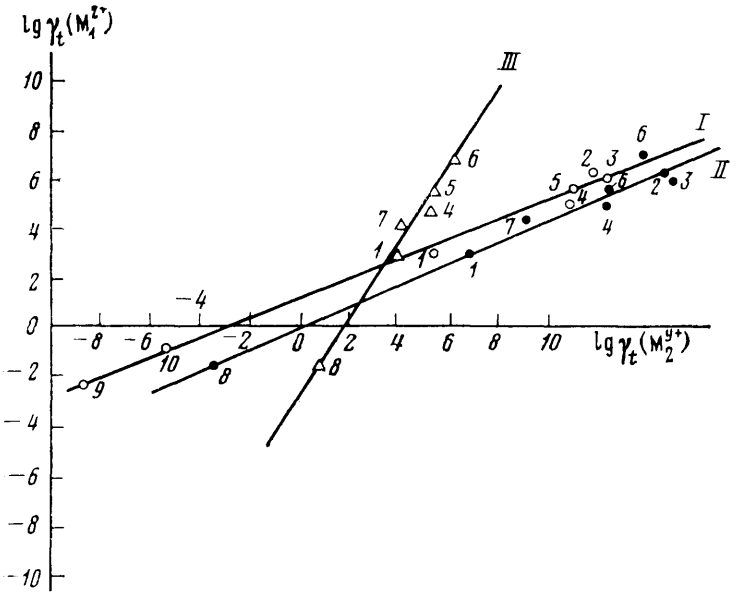


Figure 2. Dependence of $\lg\gamma_t(M_1^{z+})$ on $\lg\gamma_t(M_2^{y+})$ for ion pairs: I) Ag^+–Hg^{2+}; II) Ag^+–Hg_2^{2+}; III) Ag^+–Tl^+; solvent: 1) ethylene glycol; 2) pyrrolidone; 3) *N*-methylpyrrolidone; 4) dimethylformamide; 5) dimethylacetamide; 6) dimethyl sulphoxide; 7) *N*-methylacetamide; 8) propylene carbonate; 9) nitromethane; and 10) acetic acid.

silver complexes. Methods of comparative calculation can be used also for the approximate estimation of the activity coefficients for the transfer of Hg_n^{2+}, Ag^+, and Tl^+ ions. Some of these relations are illustrated in Fig. 2. The literature data are particularly numerous for silver ions; the use of relations analogous to those shown makes it possible to estimate not only the stability constants of the complexes and the ionic activity coefficients but also the stability constants of the solvato-complexes and the standard potentials of the mercury systems.

The results presented indicate an extremely vigorous development in recent years of the chemistry of mercury complexes. Apart from the wide-scale use of mercury compounds, this is associated with efforts directed towards the creation of a theory of solutions. With all the imperfection of the theoretical principles of non-aqueous titrimetry, there is no doubt that the use of quantitative characteristics of solvation processes (ionic activity coefficients) can serve as a reliable criterion for a well-founded choice of solvent. This approach to reactions involving the formation of mercury complexes leads to new possibilities, permitting the prediction of the equilibrium constants for reactions with participation of mercury compounds and the calculation of the activities of the reacting complex or simple forms of mercury.

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A New Mechanism of Nucleophilic Substitution

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A new radical-anionic chain mechanism of nucleophilic substitution at aliphatic, aromatic, and unsaturated carbon atoms is examined (the $S_{RN}1$ mechanism of nucleophilic substitution).
The bibliography includes 133 references.

CONTENTS

I.	Introduction	431
II.	$S_{RN}1$ nucleophilic substitution in aliphatic compounds	431
III.	$S_{RN}1$ nucleophilic substitution in aromatic compounds	440
IV.	$S_{RN}1$ nucleophilic substitution at an olefinic carbon atom	444
V.	General considerations concerning the mechanism	445

I. INTRODUCTION

According to the classification of Ingold and Hughes [1], nucleophilic substitution at a saturated carbon atom can take place via two mechanisms: the synchronous S_N2 mechanism and the two-stage S_N1 mechanism. However, in recent years it has become evident that between these limiting cases there is a possibility of a whole "spectrum" of mechanisms [2,3] and that different ionic intermediates can participate in each of these [4]. In nucleophilic aromatic substitution the specific features of the aromatic system are observed, being manifested primarily by the absence of the simple S_N2 mechanism. Nucleophilic aromatic substitution, which requires the presence of electron-accepting groups in the aromatic ring, usually takes place in stages and involves the formation of σ-anionic complexes. However, instances of S_N1 processes, leading to the formation of aryl cations, are also known.

A new type of nucleophilic substitution, involving a radical-anionic chain mechanism with formation of a substrate radical-anion and a nucleophilic radical, was discovered in 1966 in saturated systems and in 1970 in aromatic systems, and was called the $S_{RN}1$ mechanism (radical, nucleophilic, unimolecular substitution [5]). The term "radical" reflects the nature of the reaction and the term "nucleophilic" reflects its result. As regards the definition of the term "unimolecular", the authors see here an analogy (which, incidentally, is not supported by kinetic data) with S_N1 reactions, with the sole difference that the C–X bond is broken in a radical anion and not in a neutral molecule.

II. $S_{RN}1$ NUCLEOPHILIC SUBSTITUTION IN ALIPHATIC COMPOUNDS

The radical-anionic chain mechanism of nucleophilic substitution in aliphatic compounds was finally formulated in 1966 [6-9] (see the relevant reviews [10-12]) on the basis of previous (starting from the 1950s) vigorous studies on the chemistry of ambident ions. It was established that, although in principle the interaction of salts of aliphatic nitro-compounds with alkyl halides can involve alkylation

both at carbon and oxygen, the main result is the *O*-alkylation reaction[10,11]

$$RR'\bar{C}-NO_2 \leftrightarrow RR'C=NO_2^- \xrightarrow{R''CH_2X} \begin{cases} \longrightarrow RR'C(NO_2)CH_2R'' \\ \longrightarrow RR'C=N(O)OCH_2R'' \rightarrow (RR'C=NOH + R''CHO) \end{cases}$$

The nitronic esters formed subsequently decompose with formation of an oxime and an aldehyde.

However, somewhat unexpectedly, considerable amounts of *C*-alkylation products are formed in this reaction from *o*- and *p*-nitrobenzyl chlorides and also from 2,4-dinitrobenzyl chloride; thus, on interaction with the sodium salt of 2-nitropropane, *o*-nitrobenzyl chloride gives rise to 46% of the *C*-alkylation product and to 30% of the *O*-alkylation product, while the corresponding proportions of the two products obtained from the *p*-isomer are 83% and 1% (in alcohol at 30°C):[13,14]

$$p\text{-}NO_2C_6H_4CH_2Cl + (CH_3)_2\bar{C}NO_2 \cdot Na^+ \rightarrow p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 .$$

In contrast to this, benzyl chloride itself, *m*-nitrobenzyl chloride, and p-$RC_6H_4CH_2Cl$ [R = CN, CF_3, $\overset{+}{N}(CH_3)_3$, $COCH_3$, $COOCH_3$, CH_3, or Br] react only via oxygen[14].

Later it was found that the ratio of the *C*- and *O*-alkylation products depends also on the nature of the substituted group X in the *p*-nitrobenzyl system p-$NO_2C_6H_4CH_2X$ (Table 1).[15] It is noteworthy that this effect of the leaving group is not observed for the unsubstituted benzyl system: the tosylate, chloride, bromide, and iodide give an 82–84% yield of benzaldehyde.

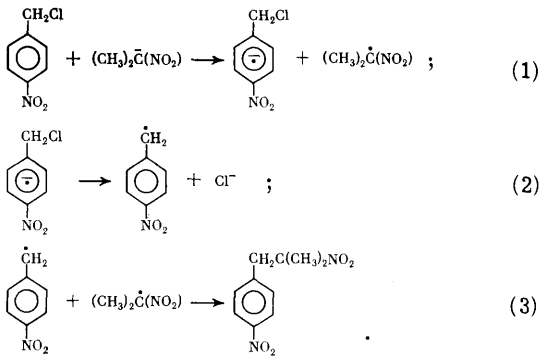
Table 1. Alkylation of the lithium salt of 2-nitropropane by the compounds p-$NO_2C_6H_4CH_2X$ in DMF at −16°C.[15]

X	Yield of product, %		Relative rate (unity for $C_6H_5CH_2X$)	X	Yield of product, %		Relative rate (unity for $C_6H_5CH_2X$)
	C-alkylation	*O*-alkylation			*C*-alkylation	*O*-alkylation	
$\overset{+}{N}(CH_3)_3Cl^-$	93	0	>100	p-$CH_3C_6H_4SO_2O$	40	32	8
C_6Cl_5COO	93	0	>100	Br	17	65	65
Cl	92	6	>100	I	7	81	3

Furthermore, the *p*-nitro-group has only a slight influence on the rate of *O*-alkylation; thus *p*-nitrobenzyl iodide, which reacts mainly via oxygen, interacts with the lithium salt of 2-nitropropane only three times as fast as benzyl iodide. On the other hand, the *p*-nitrobenzyl derivatives, which react mainly via the carbon atom [X = Cl, C_6Cl_5COO, or $\overset{+}{N}(CH_3)_3.Cl^-$], react much more vigorously than the corresponding benzyl derivatives.

It was observed that the rate of *O*-alkylation of *p*-nitrobenzyl systems p-$O_2NC_6H_4CH_2X$ (X = Cl, Br, or I) in dimethylformamide (DMF) at 0°C depends to a much greater extent on the nature of the halogen X than the rate of *C*-alkylation (Table 2).[16,17] On this basis, it was suggested that *O*-alkylation constitutes a usual S_N2-substitution, which is involved in competition with *C*-alkylation via another mechanism when groups difficult to eliminate are present.

In 1964, Kornblum and coworkers proposed for the first time a radical-ionic *C*-alkylation mechanism[16,17]:



(1)

(2)

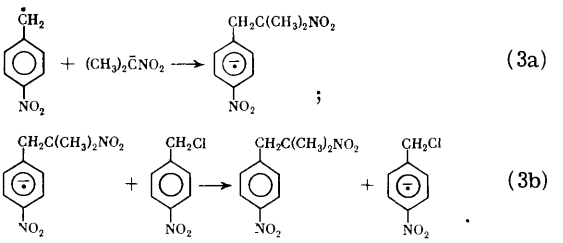
(3)

It is suggested that in the first stage an electron is transferred from the 2-nitropropane anion to *p*-nitrobenzyl chloride with formation of the radical-anion of *p*-nitrobenzyl chloride; next it decomposes with formation of the *p*-nitrobenzyl radical and the *p*-nitrobenzyl and 2-nitropropyl radicals recombine.

Table 2. Alkylation of the lithium salt of 2-nitropropane by nitrobenzyl halides in DMF at 0°C.[17]

X	Yield of product, %		Rate constant, litre mole^{-1} s^{-1}		
	C-alkylation	*O*-alkylation	overall	*C*-alkylation	*O*-alkylation
			p-$NO_2C_6H_5CH_2X$		
Cl	92	6	0.023	0.021	0.002
Br	20	80	0.34	0.068	0.27
I	8	86	1.9	0.15	1.8
			o-$NO_2C_6H_4CH_2X$		
Cl	31	52	0.0052	0.0016	0.0036
Br	1	98	0.33	0.004	0.032

Finally, in 1966 Kornblum and coworkers and independently Russell and Danen postulated a chain *C*-alkylation mechanism[6-9] having introduced stages (3a) and (3b) instead of stage (3):



(3a)

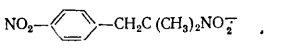
(3b)

The proposed mechanism was confirmed by a whole series of observations.

As already stated, the rate of *C*-alkylation is relatively insensitive to the nature of the leaving group, while the variation of the rates of *O*-alkylation in the Cl, Br, and I series is typical for substitution via the S_N2-mechanism[16,17].

Furthermore, it was known that aromatic nitro-compounds react with anions, including carbanions[18,19], to form radical-anions. Indeed, when the lithium salt of 2-nitropropane was added to a solution of nitrobenzene in DMF, a distinct EPR spectrum of the nitrobenzene radical-anion was produced. However, *p*-nitrobenzyl chloride at −50°C gave only an unresolved EPR signal with a width of 30 G.[16,17] Russell and Danen were able to generate *m*-nitrobenzyl chloride and *p*-nitrobenzyltrimethylammonium bromide radical-anions in ethylene by interaction with the 2-nitropropane anion under irradiation ($\lambda > 300$ nm); however, under these conditions *p*-nitrobenzyl chloride gave rise only to the EPR spectrum of the radical-anion of the reaction product—2-methyl-2-nitro-1-(*p*-nitrophenyl)propane[9].

The authors[6-9] of the proposed mechanism emphasised that stage (3a)—the interaction of the radical with the anion leading to the radical-anion—constitutes a fundamentally new type of reaction. In their discussion of the structure of the radical formed in this stage, Russell and Danen proposed an alternative structure with the localisation of the unpaired electron at the nitro-group of the side chain:



This radical-anion can isomerise rapidly to an aromatic radical-anion via an intramolecular or intermolecular mechanism, for example, as a result of the reversability of stage (3b), or it can enter stage (3b) directly before isomerising[9]. *o*-Nitrobenzyl chloride reacts via the radical-anionic mechanism with more difficulty; similarly, *o*-nitrotoluene undergoes one-elctron reduction with more difficulty than does *p*-nitrotoluene[20].

Table 3. The influence of added aromatic nitro-compounds on the interaction of *p*-nitrobenzyl chloride and the lithium salt of 2-nitropropylene in DMF at 0°C.[17]

Inhibitor (equiv.)	Yield of product, %	
	C-alkylation	*O*-alkylation
—	92	6
$C_6H_5NO_2$ (4)	84	7
m-DNB (1)	61	29
m-DNB (2)	40	48
p-DNB (0, 2)	6	88
p-DNB (1)	2	72

An extremely important piece of evidence in support of the intermediate formation of the *p*-nitrobenzyl chloride radical-anion is the fact that the addition of aromatic nitro-compounds sharply inhibits *C*-alkylation, while the rate of *O*-alkylation hardly changes; thus the rate of reaction of *p*-nitrobenzyl chloride (0.01 M) with the lithium salt of 2-nitropropane (0.02 M) in DMF at 0°C diminishes after the addition of 0.01 M *p*-dinitrobenzene (*p*-DNB) by a factor of ten[17] (see also Table 3). This inhibiting influence can be explained by the fact that aromatic nitro-compounds react rapidly with *p*-nitrobenzyl chloride radical-anions, regenerating the initial *p*-nitrobenzyl chloride and thereby preventing *C*-alkylation. The inhibiting capacity varies in proportion to the electron affinity of the aromatic nitro-inhibitor (*p*-DNB > *m*-DNB > $C_6H_6NO_2$), which agrees with the series based on the relative reactivities of these compounds in electrochemical reduction: the polarographic reduction potentials in acetonitrile at 25°C are −0.69, −0.90, and −1.15 V for *p*-DNB, *m*-DNB, and nitrobenzene respectively[21].

Naturally, the inhibitors can react also with the radical-anions of the reaction products formed in stage (3a), blocking stage (3b) thereby and terminating the chain.

It is also known that aromatic nitro-compounds are effective inhibitors of free-radical chain processes[22,23] in which only neutral radicals participate, and, although the mechanism of such inhibition is not altogether clear, there is a possibility of the blocking of the proposed mechanism as a result of the interaction of the inhibitor with *p*-nitrobenzyl radicals. The inhibiting influence of hexaphenylethane is almost certainly due to the interaction of *p*-nitrobenzyl radicals with triphenylmethyl radicals[8,9].

C-Alkylation is fully inhibited in the presence of molecular oxygen; instead the 2-nitropropane anion is oxidised to acetone and the nitrite ion[24]:

$$(CH_3)_2\dot{C}(NO_2) + O_2 \rightarrow (CH_3)_2C(NO_2)-OO^{\cdot},$$
$$(CH_3)_2C(NO_2)-OO^{\cdot} + (CH_3)_2\bar{C}(NO_2) \rightarrow (CH_3)_2C(NO_2)-OO^{-} + (CH_3)_2\dot{C}(NO_2),$$
$$(CH_3)_2C(NO_2)-OO^{-} + (CH_3)_2\bar{C}(NO_2) \rightarrow 2(CH_3)_2C(NO_2)-O^{-},$$
$$(CH_3)_2C(NO_2)O^{-} \rightarrow (CH_3)_2CO + NO_2^{-}.$$

In the absence of *p*-nitrobenzyl chloride the 2-nitropropane anion is resistant to the action of oxygen.

The finding that the alkylation of the anion of 2-ethoxycarbonyl-3-coumaranone, which usually proceeds via the S_N2-mechanism and gives rise to considerable amounts of *O*-alkylation products, takes place almost exclusively as *C*-alkylation when *p*-nitrobenzyl chloride is used[6,7]:

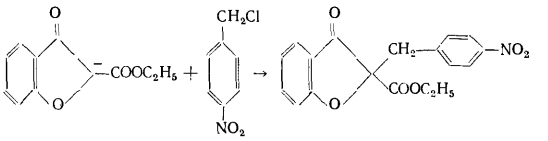


Table 4. Alkylation of the sodium salt of 2-ethoxycarbonyl-3-cumaranone by benzyl halides in DMF at 0°C.[6]

X	Yield of product, %		10^4k, litre mole^{-1} s^{-1}		
	C-alkylation	*O*-alkylation	overall	*C*-alkylation	*O*-alkylation
			$C_6H_5CH_2X$		
Cl	40	50	0.08	0.03	0.04
Br	64	29	13	8	4
I	72	18	200	144	36
			m-$NO_2C_6H_4CH_2X$		
Cl	40	52	0.19	0.06	0.10
Br	65	28	49	32	14
I	73	18	440	320	79
			p-$NO_2C_6H_4CH_2X$		
Cl	90	2	30	27	0.6
Br	66	24	53	35	13
I	74	19	440	325	75

The ratios of the rates of *C*-alkylation for $C_6H_5CH_2X$, m-$O_2NC_6H_4CH_2X$, and p-$O_2NC_6H_4CH_2X$ are 1 : 4 : 4 when X = Br and 1 : 2 : 2 when X = I. On the other hand, when X = Cl, the rate of reaction for the *p*-nitrobenzyl system increases sharply and the ratios become 1 : 2 : 900 (Table 4).[6] Only this last reaction is suppressed by the addition

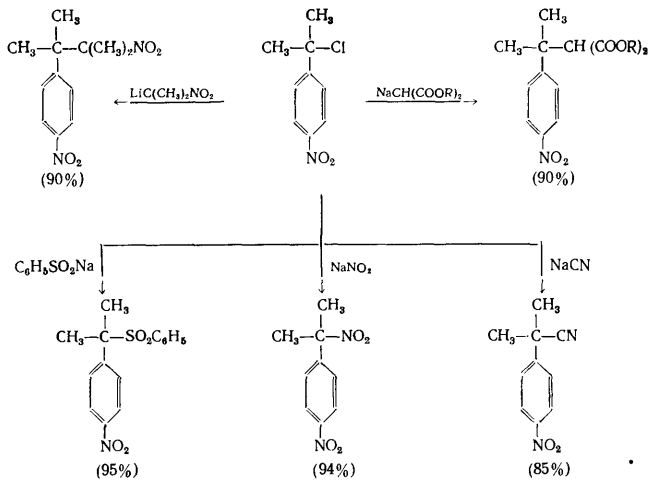
of *m*- and *p*-DNB (Table 5), while the addition of copper(II) chloride (6×10^{-6} mole) decreases the rate constant for alkylation by *p*-nitrobenzyl chloride from 3×10^{-3} to 5×10^{-5} litre mole^{-1} s^{-1} and alters the yield of the *C*- and *O*-alkylation products from 90 and 2% to 45 and 48% respectively[7].

Table 5. The influence of added inhibitors on the reaction of *p*-nitrobenzyl chloride with the sodium salt of 2-ethoxycarbonyl-3-cumaranone in DMF at 20°C.[6]

Inhibitor (equiv.)	Yield of product, %		$\tau_{1/2}$, h
	C-alkylation	*O*-alkylation	
—	90	2	0.5
C_6Cl_6 (2)	67	24	2
$PhNO_2$ (2)	67	26	3
m-DNB (2)	58	36	3
p-DNB (0.1)	47	42	4
p-DNB (1)	46	49	6
p-DNB (2)	44	46	7

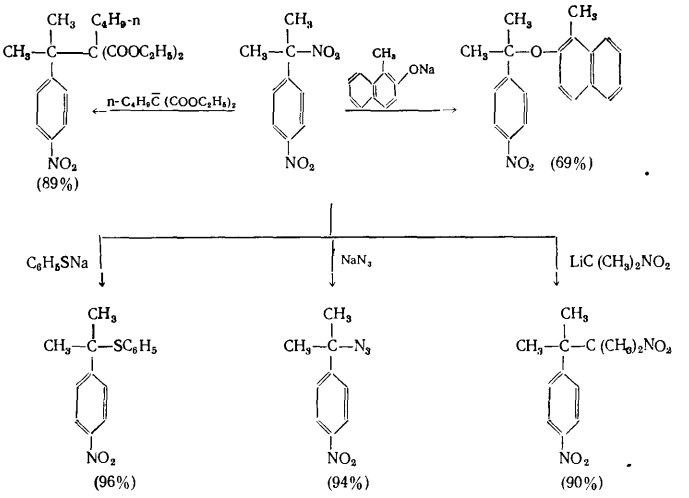
The successful study of the radical-anionic chain mechanism was continued by investigating substitution at a tertiary carbon atom in the *p*-nitrocumenyl system. This system has many advantages compared with the *p*-nitrobenzyl system. When tertiary halides are used, the competing S_N2-substitution mechanism is almost completely excluded. Also excluded is the side reaction of the bases with the fairly acidic products of the methylene group of the benzyl halide (for example, in the reaction of *p*-nitrobenzyl chloride with sodium 1-methyl-2-naphthoxide up to 40% of *p*,*p*′-dinitrostilbene is formed together with the *O*- and *C*-alkylation products).

It was found that *p*-nitrocumenyl chloride reacts exceptionally readily with various nucleophiles at room temperature in an inert gas atmosphere giving a high yield of the substitution product[25]:



Primary, secondary, and tertiary amines readily react with *p*-nitrocumenyl chloride to form alkylation products in high yields (Table 6)[26].

Such ease of substitution at a tertiary carbon atom is very striking. Even more surprising is the finding that α,*p*-dinitrocumene reacts easily with a wide variety of nucleophiles[27]:



Before Kornblum's investigation, no examples of the substitution of the nitro-group at a saturated carbon atom were known. Naturally, neither cumenyl chloride nor α-nitrocumene undergo these reactions.

Table 6. The reaction of *p*-nitrocumenyl chloride with amines (in DMSO, in the light, in N_2 atmosphere, ~35°C).[26]

Amine	Reaction time, h	Yield, %	Amine	Reaction time, h	Yield, %
Quinuclidine	10	90	Di-n-butylamine	88	34
Diazabicyclo-octane	36	85	Methylamine	5	91
Piperidine	18	91	Dimethylamine	5	96
Pyrrolidine	16	90	Trimethylamine	22	66
n-Butylamine	90	67	Ammonia	428	27

It is noteworthy that reactions of this type are relatively insensitive to steric hindrance and can be used successfully to synthesise sterically hindered compounds. In fact the first stage (electron transfer) involves only the aromatic nitro-component of the molecule. The second stage (conversion of the radical-anion into a radical as a result of the elimination of the leaving group) is also insensitive to the influence of steric factors. The third stage involves addition to the planar system of the radical; a combination of minimal steric requirements with a high reactivity of the radical ensures the ease of this stage also. Finally, the last stage (electron transfer from the aromatic nitro-radical-anion to the nitroarene) is very rapid and probably proceeds with minimal steric requirements[11].

Subsequent, detailed studies confirmed each stage of the proposed mechanism. At the beginning of these investigations the inhibiting influence of molecular oxygen was already noted[16-17,25-29] (Table 7). Thus the reaction of *p*-nitrocumenyl chloride with sodiomalonic ester in argon gives the *C*-alkylation product in 95% yield, while

in the presence of oxygen the alkylation is completely suppressed and *p*-nitrocumenyl alcohol is formed in 94% yield. Similarly the reaction of α,*p*-dinitrocumene with sodiobutylmalonic ester in argon gives a 98% yield of the *C*-alkylation product, while in the presence of oxygen *C*-alkylation proceeds to an extent of only 6% and *p*-nitrocumenyl alcohol is formed in 80% yield. In the absence of anions neither *p*-nitrocumenyl chloride nor α,*p*-dinitrocumene react with oxygen. Oxygen influences similarly the reaction of *p*-nitrocumenyl systems with amines[26].

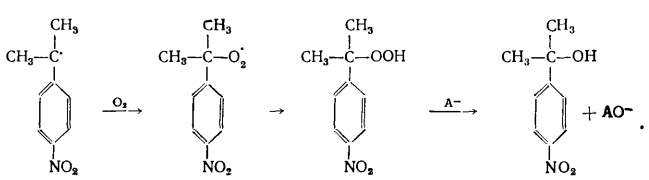
Table 7. The inhibiting influence of molecular oxygen on the reactions of *p*-nitrocumenyl chloride with nucleophiles (in DMSO).[29]

Anion	Atmosphere	Yield, %	
		substitution product	*p*-$NO_2C_6H_4C(CH_3)_2OH$
$C_4H_9\bar{C}(COOC_2H_5)_2$	N_2	89	0
$C_4H_9\bar{C}(COOC_2H_5)_2$	O_2	0	88
$\bar{C}H(COOC_2H_5)_2$	Ar	95	0
$\bar{C}H(COOC_2H_5)_2$	O_2	0	94
1-Methyl-2-naphthoxide	Ar	63	30*
1-Methyl-2-naphthoxide	O_2	0	66
$C_6H_5S^-$	Ar	95	0
$C_6H_5S^-$	O_2	4	83
$(CH_3)_2\bar{C}NO_2$	Ar	85	10
$(CH_3)_2\bar{C}NO_2$	O_2	20	70
N_3^- ***	N_2	97	0
N_3^- ***	O_2	63	20**
$C_6H_5SO_2^-$ ***	N_2	97	0
$C_6H_5SO_2^-$ ***	O_2	0	72

* *p*-$NO_2C_6H_4C(CH_3)=CH_2$.
** *p*-$NO_2C_6H_4C(CH_3)_2OOH$.
*** In HMPA.

When the reactions with sodium azide and piperidine are carried out in hexamethylphosphoramide (HMPA), it is possible to isolate *p*-nitrocumenyl hydroperoxide and not *p*-nitrocumenyl alcohol; thus the hydroperoxide is formed in 76% yield in the reaction of sodium azide with α,*p*-dinitrocumene in the presence of oxygen.

The mechanism of the inhibiting action of oxygen now becomes clear. Oxygen reacts with *p*-nitrocumenyl radicals, forming peroxy-radicals, which abstract hydrogen from the solvent and are converted into *p*-nitrocumenyl hydroperoxide. The anions (with the exception of the azide ion) rapidly reduce the hydroperoxide to the alcohol:



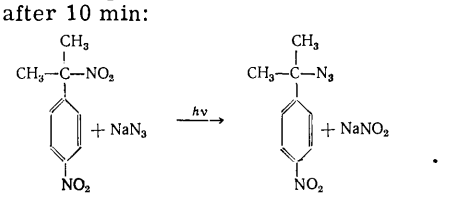
A^- represents an anion with reducing properties. In dimethylsulphoxide (DMSO) the solvent can also behave as the reducing agent[30].

The influence of the presence of traces of oxygen on the rate of reaction shows that it has a chain mechanism. Thus *p*-nitrocumenyl chloride reacts with sodium benzenesulphinate almost quantitatively with formation of the corresponding sulphone. In nitrogen at 25°C the reaction takes place over a period of 2 h, while in the presence of oxygen (1 mole %) only 10% of the substance reacts during this period. Analogous observations were made in the reactions with quinuclidine[26], sodiomalonic ester, the lithium salt of 2-nitropropane, and sodium azide[29].

As already stated above, the inhibiting influence of nitroarenes (*p*- and *m*-DNB) on the *C*-alkylation of the 2-nitropropane anion has been explained by the rapid electron transfer from the *p*-nitrobenzyl chloride radical-anion to the nitroarene, while the rate of *O*-alkylation via the S_N2-mechanism does not change under these conditions. *p*-Nitrocumenyl chloride cannot react via the S_N2 mechanism and the reaction is therefore simply retarded when nitroarenes are added. Thus the interactions of *p*-nitrocumenyl chloride with sodium azide, which takes place to an extent of 65% in 75 s, and with sodium nitrite, which is 93% complete after 20 min, are fully suppressed by the addition of *p*-DNB (10 mole %); the reaction with sodium benzene sulphinate, which takes place to an extent of 83% in 5 min, is only 19% complete after this period following the addition of *m*-DNB (10 mole %).[11] These results indicate the intermediate formation of radical-anions from the *p*-nitrocumenyl systems and a chain mechanism of the process.

Di-t-butylnitroxyl has also been used as a radical trap[31]. The reactions of *p*-nitrocumenyl chloride with the lithium salt of 2-nitropropane and quinuclidine, which proceed to an extent of 90% in 30 min and 61% in 5 h respectively, proceed to an extent of only 3–4% in the presence of 5 mole % of di-t-butylnitroxyl, while the reaction of α,*p*-dinitrocumene with sodium benzenesulphinate (20 min, 48%) is fully suppressed; galvinoxyl has a similar effect[11].

At the very beginning of studies on the radical-anionic chain mechanism the activating influence of illumination on the rate of the process was already established, diffuse daylight or the light of a fluorescent lamp being frequently sufficient[8,9,25–27]. Thus α,*p*-dinitrocumene does not react with sodium azide in the dark over a period of 2 days; under the influence of daylight, the extent of reaction after 30 min is 63% and under illumination by light from two 20-watt lamps at a distance of 15 cm the reaction is complete after 10 min:



The quantum yields of this reaction and the analogous reaction with *p*-nitrocumenyl chloride are 570 and 600, which undoubtedly indicates a chain mechanism of these processes. It is noteworthy that illumination is not always necessary for the reaction but frequently accelerates it. The study of the influence of the wavelength on the quantum yield shows that illumination promotes the formation of a charge-transfer complex of the nucleophile and the *p*-nitrocumenyl system [stage (1)].[11]

The hypothesis of the activating influence of light on stage (2) of the mechanism is less likely. Also unlikely is the following mechanism of stage (1): the nitro-compound undergoes $n \rightarrow \pi^*$ excitation under the influence of

light and abstracts hydrogen from the solvent, whereupon the base abstracts a proton with formation of a radical-anion [32-34]:

$$p\text{-}NO_2C_6H_4CR_2Cl \xrightarrow[\text{solvent}]{h\nu} [p\text{-}ClCR_2C_6H_4NO_2H^{\cdot}] \xrightarrow{B^-} p\text{-}ClCR_2C_6H_4NO_2^{\cdot-} .$$

The proposed reaction mechanism (see above) shows that the nucleophile plays a dual role in stages (1) and (3a) of the process. In stage (1) it plays the role of a one-electron reductant of the *p*-nitrobenzyl (*p*-nitrocumenyl) system. In stage (3a) the nucleophile, which propagates the reaction chain, adds to the *p*-nitrobenzyl (*p*-nitrocumenyl) radical. Presumably not only the anions which initiated the radical chain but also the anions which are not effective one-electron reductants of these systems react with radicals at this stage. In other words, the catalytic amount of the nucleophile capable of chain initiation is sufficient for the reaction between nucleophiles inactive in this respect and, for example, *p*-nitrocumenyl chloride or α,p-dinitrocumene. Indeed, this effect has been observed (Table 8). [35] Thus, whereas α,p-dinitrocumene does not react with sodium azide in the dark over a period of 48 h, the addition of 5 mole % of the lithium salt of 2-nitropropane leads to the formation of the corresponding azide in 97% yield after only 3 h. *p*-Nitrocumenyl chloride and sodium nitrite do not react in the dark over a period of 90 min; the addition of 5 mole % of the same initiator makes it possible to obtain 93% of α,p-dinitrocumene in 90 min. The reaction of *p*-nitrocumenyl chloride with quinuclidine is very slow in the dark, but the addition of 7 mole of the initiator makes it possible to obtained the corresponding salt in 63% yield after 36 h:

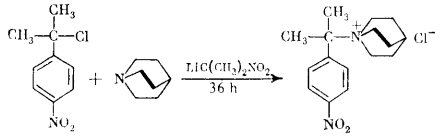


Table 8. Reactions of α,p-dinitrocumene with anions initiated by the lithium salt on 2-nitropropane (in HMPA in the dark) [35].

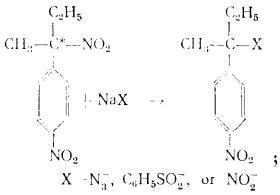
Anion	Amount of initiator, mole %	Reaction time, h	Degree of reaction, %	Product*	Yield, %
$(CH_3)_2\bar{C}NO_2$	—	3	37	$RC(CH_3)_2NO_2$	71
N_3^-	—	48	0	RN_3	0
N_3^-	5	3	100	RN_3	97
$C_6H_5SO_2^-$	—	96	8	$RSO_2C_6H_5$	8
$C_6H_5SO_2^-$	0.8	4	77	$RSO_2C_6H_5$	75
$C_6H_5SO_2^-$	5	4	100	$RSO_2C_6H_5$	95
$\bar{C}H(COOC_2H_5)_2$	—	12	26	$RCH(COOC_2H_5)_2$	26
$\bar{C}H(COOC_2H_5)_2$	5	12	53	$RCH(COOC_2H_5)_2$	51

*R = *p*-nitrocumenyl.

Although the 2-nitropropane anion is a fairly effective initiator, other anions also have this capacity and the azide ion, which does not react with α,p-dinitrocumene in the dark, initiates the reaction with sodium benzenesulphinate in the light [35]. The observed series of induced reactions confirms the proposed mechanism and extends the synthetic scope of reactions via this mechanism.

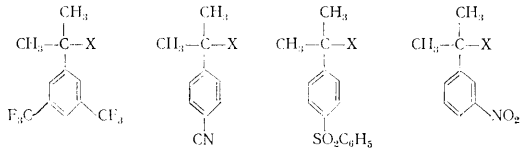
It is quite natural that not only reducing nucleophiles, but also typical one-electron transferring agents can induce reactions with relatively inactive nucleophiles [11]. Thus the reaction between α,p-dinitrocumene and sodium azide in the dark is initiated by the addition of 5 mole % of sodionaphthalene, 3 mole % of sodium-trimesitylboron, and 4 mole % of a solution of sodium in HMPA (the yields of *p*-nitrocumenyl azide after 30 min are 97, 92, and 87% respectively). *p*-Nitrocumenyl chloride, which reacts slowly with sodium nitrite in the dark in HMPA (6% after 90 min), is converted into α,p-dinitrocumene during this period in yields of 89 and 85% after the addition of 12 mole % of sodionaphthalene and 20 mole % of a solution of sodium in HMPA ("solvated electron") respectively.

The radical mechanism of the reaction was confirmed in a study of the stereochemistry of the substitution: when optically active α-methylpropyl-α,p-dinitrobenzene reacts with sodium azide, benzenesulphinate, or thiophenoxide in HMPA, the racemic azide, sulphone, or thioether are formed. Naturally the interaction with sodium nitrite also leads to the racemisation of the initial compound [11]:

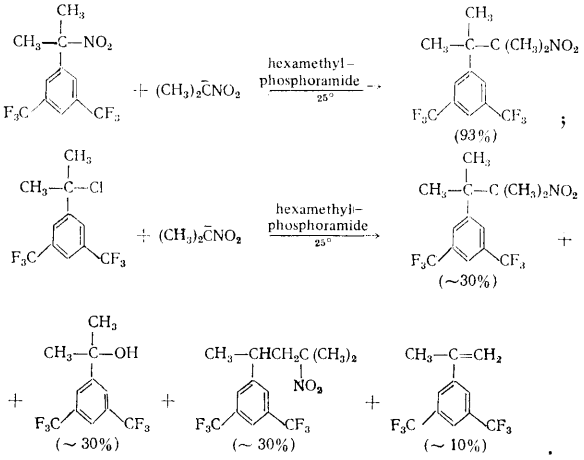


X = N_3^-, $C_6H_5SO_2^-$, or NO_2^-.

Vigorous attempts have now been made to extend the range of organic compounds capable of involvement in radical-anionic chain substitution reactions. Several cumenyl systems containing electron-accepting substituents in the benzene ring have been found [11]:



Although a whole series of synthetically valuable reactions have been observed for these systems, they are fairly frequently accompanied by side processes which do not occur with *p*-nitrocumenyl systems and this can be undoubtedly accounted for by the different stabilities of the corresponding radical-anions and radicals. This hinders routine applications of the radical-anionic chain substitution reactions for synthetic purposes:



Thus, whereas α-nitro-3,5-bis(trifluoromethyl)cumene smoothly alkylates the 2-nitropropane anion at a carbon atom with a yield of 93%, 3,5-bis(trifluoromethyl)cumenyl chloride gives the same product with a yield of only 30%. Two competing side reactions takes place: (a) *O*-alkylation via the S_N2 mechanism with subsequent formation of 3,5-bis(trifluoromethyl)cumenyl alcohol; (b) dehydrochlorination with formation of α-methyl-3,5-bis(trifluoromethyl)styrene and subsequent Michael addition to the latter of the 2-nitropropane anion [11].

Like the *p*-nitrocumenyl system, the *m*-nitrocumenyl system gives high yields of *C*-alkylation products in the reactions with sodium thiophenoxide, sodiomalonic ester, and sodiobutylmalonic ester, but in the reaction of *m*-nitrocumenyl chloride with ambident ions the formation of considerable amounts of *O*-alkylation products (S_N2 reaction) is observed [28]. Thus the reaction of *m*-nitrocumenyl chloride with sodium nitrite gives 52% of α,*m*-dinitrocumene and 27% of *m*-nitrocumenyl alcohol; under the same conditions, the *p*-isomer is converted to an extent of 92–95% into α,*p*-dinitrocumene. The reaction of the lithium salt of 2-nitropropane with *m*-nitrocumenyl chloride in HMPA leads to the formation of 33% of the *C*-alkylation product, 35% of *m*-nitrocumenyl alcohol, and 15% of *m*-nitromethylstyrene; the reaction with sodium benzenesulphinate gives 59% of the sulphone and 11% of *m*-nitrocumenyl alcohol, while *p*-nitrocumenyl chloride or α,*p*-dinitrocumene give rise only to the corresponding sulphone in 97% yield. Oxygen almost completely inhibits substitution via the radical-anionic mechanism in *p*-nitrocumenyl systems and leads to the formation of *p*-nitrocumenyl alcohol, whereas such inhibition of the reaction of *m*-nitrocumenyl chloride is not so pronounced and *m*-nitrocumenyl alcohol is formed in small amounts (Table 9) [28]. On the basis of these observations, it is suggested [28] that a non-chain radical "cage" mechanism can play an important role for *m*-nitrocumenyl chloride:

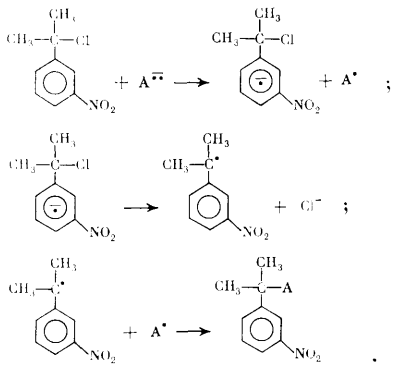


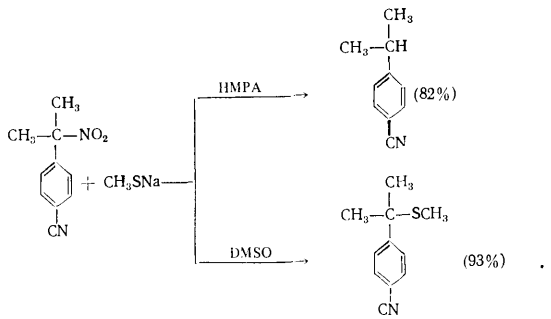
Table 9. The inhibiting influence of oxygen on the reaction of *m*-nitrocumenyl chloride with anions (in DMSO). [28]

Anion	Atmosphere	Yield of products, %		
		substitution product	m-$NO_2C_6H_4C(CH_3)_2OH$	initial substance
$\bar{C}H(COOC_2H_5)_2$	Ar	92	0	—
$\bar{C}H(COOC_2H_5)_2$	O_2	70	3	22
$C_6H_5S^-$	N_2	94	0	—
$C_6H_5S^-$	O_2	82	2	12
N_3^- *	N_2	79	0	6
N_3^- *	O_2	76	0	14

* In HMPA.

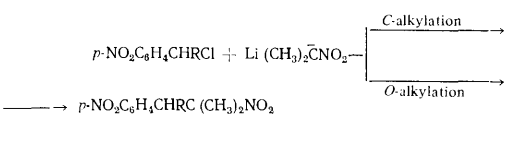
Incidentally, the absence of selectivity in the alkylation of ambident anions by *m*-nitrocumenyl chloride can be explained with the aid of this mechanism.

The reaction of *p*-cyano-α-nitrocumene with sodium methanethiolate in DMSO gives the corresponding sulphide in 93% yield, while in HMPA the product is *p*-cyanocumene in 82% yield [11]:



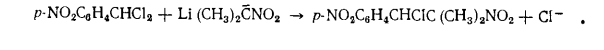
In view of the similarity of the electron-accepting properties of the *p*-nitrophenyl and γ-pyridyl residues, 2-nitro-γ-pyridylpropane evidently interacts with the 2-nitropropane anion via a radical-anionic mechanism [11]. Light accelerates the reaction, while the addition of 5 mole % of *m*-DNB or di-t-butyl nitroxide fully inhibits it.

Although Kornblum [11] frequently emphasised and demonstrated the relative insensitivity of the *C*-alkylation via the radical-anionic mechanism to steric requirements (say in relation to *p*-nitrocumenyl systems), in 1976 Norris and Randles [36] showed that this is not always the case. By studying the interaction of α-alkyl-*p*-nitrobenzyl chlorides (R = CH_3, C_2H_5, iso-C_3H_7, or t-C_4H_9) with the lithium salt of 2-nitropropane, they showed, that, when R = CH_3 or C_2H_5, competing $S_{RN}1$ and S_N2 processes, leading to *C*- and *O*-alkylation products, take place. For more sterically hindered chlorides (R = iso-C_3H_7 or t-C_4H_9), the reaction proceeds exclusively as *O*-alkylation despite the clear $S_{RN}1$ mechanism and only the corresponding ketones *p*-$NC_2C_6H_4COR$ are formed as a result of the decomposition of nitronic esters (Table 10):



The hypothesis that in the last two cases the S_N2 mechanism operates is disproved by a whole series of observations: the reaction in the dark is much slower than in the light, oxygen and *p*-DNB have an inhibiting effect and, finally, α-isopropyl- and α-t-butyl-benzyl chlorides do not react under the conditions indicated. According to the authors [36], steric hindrance in stage (3a) of the radical-anionic chain mechanism provides the best explanation of the results. It also explains the decrease of the rate of interaction with increasing bulk of the group R (Table 10).

p-Nitrobenzylidene chloride also reacts with the lithium salt of 2-nitropropane via the radical-anionic chain mechanism with formation of 1-chloro-2-methyl-2-nitro-1-(*p*-nitrophenyl)propane [37–39]:



The reaction is inhibited by oxygen and *p*-DNB and is accelerated under illumination (Table 11).

Table 10. The interaction of α-alkyl-*p*-nitrobenzyl chlorides with the lithium salt of 2-nitropropane in DMSO at 20°C. [36]

Alkyl	Reaction conditions	Reaction time, h	Yield of products, %		
			C-alkylation	O-alkylation	initial substance
CH_3	N_2	20	66	34	0
CH_3	N_2, $h\nu$	20	82	18	0
CH_3	O_2	20	36	57	7
CH_3	N_2 *	7	18	13	69
CH_3	N_2, $h\nu$ *	7	33	11	56
CH_3	N_2 *	23	45	19	36
CH_3	N_2, $h\nu$ *	23	81	19	0
CH_3	O_2 *	23	0	71	29
C_2H_5	N_2	30	71	29	0
C_2H_5	N_2, $h\nu$	30	80	20	0
C_2H_5	O_2	30	24	71	5
iso-C_3H_7	N_2, $h\nu$	45	0	100	0
iso-C_3H_7	N_2	24	0	56	44
iso-C_3H_7	N_2, $h\nu$	24	0	81	19
iso-C_3H_7	O_2	24	0	57	43
iso-C_3H_7	N_2 **	24	0	35	65
t-C_4H_9	N_2, $h\nu$	96	0	100	0
t-C_4H_9	N_2	54	0	64	36
t-C_4H_9	N_2, $h\nu$	54	0	88	12
t-C_4H_9	O_2	54	0	9	91
t-C_4H_9	N_2 **	54	0	27	73

*In DMF.
**In the presence of 100 mole % *p*-DNB.

Table 11. The interaction of *p*-nitrobenzylidene chloride with the lithium salt of 2-nitropropane in DMSO at 20°C. [39]

Amount of $(CH_3)_2CLiNO_2$, (equiv.)	Reaction conditions	Reaction time, min	Yield, %*		
			initial substance	A	B
2	N_2	40	11	51	16
2	N_2, $h\nu$	40	3	55	24
2	O_2	40	26	37	8
1	N_2	60	50	31	6
1	N_2 **	60	68	10	2
4	N_2, 30°	3	3	50	36
4	N_2, 30°	60	0	0	88

*Notation: A = 1-chloro-2-methyl-2-nitro-1-(*p*-nitrophenyl)propane; B = β,β-dimethyl-*p*-nitrostyrene.
**After the addition of 10 mole % *p*-DNB.

However, perhaps the most interesting fact in this connection is that the authors [38,39] observed in their study of the reaction in the presence of an excess of the nucleophile a new type of elimination reaction with participation of a radical-anion—an $E_{RC}1$ reaction (radical-chain unimolecular elimination). The secondary interaction between the reaction product and the nucleophile leads to the formation of β,β-dimethyl-*p*-nitrostyrene and 2,3-dimethyl-2,3-dinitrobutane via the mechanism

$$p\text{-}NO_2C_6H_4CHClC(CH_3)_2NO_2 + 2(CH_3)_2\bar{C}NO_2 \rightarrow$$
$$\rightarrow p\text{-}NO_2C_6H_4CH{=}C(CH_3)_2 + (CH_3)_2C(NO_2){-}C(NO_2)(CH_3)_2 + Cl^- + NO_2^-$$

and not to double substitution. The reaction is initiated by light (in DMF in the dark at 5°C it proceeds to an extent of only 8%, while under illumination its extent is 96%) and is inhibited by *p*-DNB: in DMSO in the dark at 20°C the yield of β,β-dimethyl-*p*-nitrostyrene after 150 min is 90%, while in the presence of 20 mole % of *p*-DNB the yield falls to 18%. Benzylidene chloride itself does not undergo this reaction. The authors [38,39] proposed the following mechanism for this interaction:

$$ArCHClC(CH_3)_2NO_2 + (CH_3)_2\bar{C}NO_2 \rightarrow [ArCHClC(CH_3)_2NO_2]^{\cdot-} + (CH_3)_2\dot{C}NO_2;$$
$$[ArCHClC(CH_3)_2NO_2]^{\cdot-} \xrightarrow{\text{slow}} Ar\dot{C}HC(CH_3)_2NO_2 + Cl^-;$$
$$Ar\dot{C}HC(CH_3)_2NO_2 + (CH_3)_2\bar{C}NO_2 \rightarrow ArCH{=}C(CH_3)_2 + (CH_3)_2\dot{C}NO_2 + NO_2^-;$$

or

$$Ar\dot{C}HC(CH_3)_2NO_2 + A^- \rightarrow ArCH{=}C(CH_3)_2 + NO_2^- + A\cdot;$$
$$(CH_3)_2\bar{C}NO_2 + (CH_3)_2\dot{C}NO_2 \rightarrow [(CH_3)_2C(NO_2){-}C(CH_3)_2NO_2]^{\cdot-};$$
$$[(CH_3)_2C(NO_2){-}C(CH_3)_2NO_2]^{\cdot-} + ArCHClC(CH_3)_2NO_2 \rightarrow;$$
$$\rightarrow (CH_3)_2C(NO_2){-}C(NO_2)(CH_3)_2 + [ArCHClC(CH_3)_2NO_2]^{\cdot-}.$$

It is of interest to note that *p*-nitrobenzylidene acetate also interacts with the lithium salt of *p*-nitropropane, forming 2-methyl-2-nitro-1-(*p*-nitrophenyl)propyl acetate:

$$p\text{-}NO_2C_6H_4CH(OCOCH_3)_2 + (CH_3)_2\bar{C}NO_2 \rightarrow p\text{-}NO_2C_6H_4CH(OCOCH_3)C(CH_3)_2NO_2.$$

However, a completely different, ionic-chain (and not radical-chain) mechanism operates here: in the first stage the diacetate undergoes nucleophilic cleavage with formation of the free aldehyde [37,40]. The reaction is insensitive to light, oxygen, and *p*-DNB, and both benzylidene acetate itself and other $ArCH(OCOCH_3)_2$ undergo this reaction.

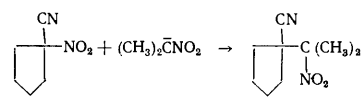
The reactions of (4-nitrobenzyl)- and (4-nitrophenyl)-methyl halides with the t-butoxide ion in t-butyl alcohol, which lead to high yields of 4,4′-dinitrostilbene and 4,4′-dinitrotetraphenylethylene respectively, also proceed via the radical-ionic chain mechanism [41]:

$$ArCH_2X + t\text{-}C_4H_9O^- \rightleftarrows Ar\dot{C}HX + t\text{-}C_4H_9OH;$$
$$ArCH_2X + t\text{-}C_4H_9O^- \rightarrow ArCH_2X^{\cdot-} + t\text{-}C_4H_9O\cdot;$$
$$ArCH_2X^{\cdot-} \rightarrow ArCH_2^{\cdot} + X^-$$
$$ArCH_2^{\cdot} + Ar\bar{C}HX \rightarrow [ArCH_2CHXAr]^{\cdot-}$$
$$[ArCH_2CHXAr]^{\cdot-} + ArCH_2X \rightleftarrows ArCH_2X^{\cdot-} + ArCH_2CHXAr$$
$$ArCH_2CHXAr + t\text{-}C_4H_9O^- \rightarrow ArCH{=}CHAr + t\text{-}C_4H_9OH + X^-.$$

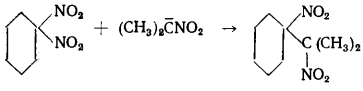
The radical-ionic chain mechanism has been considered as one of the possibilities for the reaction of benzyl halides with sodium thiolates in which the formation of benzyl and thiyl radicals was demonstrated [42].

The range of substitution reactions involving radical-anions was extended in 1970 when Kornblum and coworkers found that the anions of nitro-compounds can react with α-nitrocarbonyl compounds (esters and ketones), α-nitronitriles, and α,α-dinitro-compounds, displacing the nitro-group [43,44]:

$$(CH_3)_2C(NO_2)COOC_2H_5 + (CH_3)_2\bar{C}(NO_2) \xrightarrow[\sim 20°]{DMSO} (CH_3)_2C(COOC_2H_5){-}C(NO_2)(CH_3)_2 \quad (95\%);$$
$$(CH_3)_2C(NO_2)COC_6H_5 + (CH_3)_2\bar{C}NO_2 \rightarrow (CH_3)_2C(COC_6H_5){-}C(NO_2)(CH_3)_2 \quad (82\%);$$



(84%);



(91%).

Further studies confirmed the radical-anionic chain mechanism of these reactions†. Thus light accelerates the reaction and, when the wavelength of the initiating

† It is of interest to note that the nitro-group can be substituted under the influence of the *p*-thiocresolate ion in primary and secondary nitro-compounds under the conditions of the usual S_N2 mechanism [45].

light is 400 nm, the quantum yield of ethyl α-nitroisobutyrate is 220; ethyl α-chloroisobutyrate does not react with the lithium salt of 2-nitropropane, while the α-bromoester gives rise to a complex range of products, from which the *C*-alkylation product was isolated in a yield of only 9%.[43,44]

Sodionaphthalene is an effective catalyst of the reaction of 2,2-dinitropropane with the anion of 2-nitropropane[46]:

$$(CH_3)_2C(NO_2)_2 + (CH_3)_2\bar{C}NO_2 \xrightarrow{C_{10}H_8Na} (CH_3)_2C(NO_2)-C(NO_2)(CH_3)_2 .$$

Inhibitors of radical processes strongly retard the reaction of ethyl α-nitroisobutyrate, α-nitroisobutyrophenone, and α,α-dinitrocyclohexane with the lithium salt of 2-nitropropane[44]. A complete analogy is observed in this case between the first two stages of the mechanism of the above reactions (one-electron reduction of α-nitrocompounds with subsequent decomposition of the resulting radical-anion into a radical and a nitrite ion) and the previously investigated behaviour of aliphatic nitro-compounds under the influence of more vigorous reductants, such as metallic sodium and the electric current[47,48].

The anions of nitroalkanes are not the only species which can displace the nitro-group from α,α-dinitrocompounds. Thus, 2,2-dinitropropane reacts at 25°C, albeit fairly slowly, with sodium benzenesulphinate to give the corresponding sulphone in 81% yield[49]:

$$(CH_3)_2C(NO_2)_2 + C_6H_5SO_2^- \xrightarrow[25^\circ]{3\ days} (CH_3)_2C(NO_2)SO_2C_6H_5 .$$

The reaction is accelerated under illumination and is fully inhibited by the addition of 10 mole % of di-t-butylnitroxyl.

The reaction between 2,2-dinitropropane and sodioethylmalonic ester is accelerated by irradiation with light or by the addition of 15 mole % of the potassium derivative of nitrobenzene:

$$(CH_3)_2C(NO_2)_2 + C_2H_5\bar{C}(COOC_2H_5)_2 \xrightarrow{DMF} (CH_3)_2C(NO_2)-C(C_2H_5)(COOC_2H_5)_2 .$$

Irradiation also accelerates the reaction between 2,2-dinitropropane and sodioethylacetoacetic ester or sodiomethylacetylacetone[46].

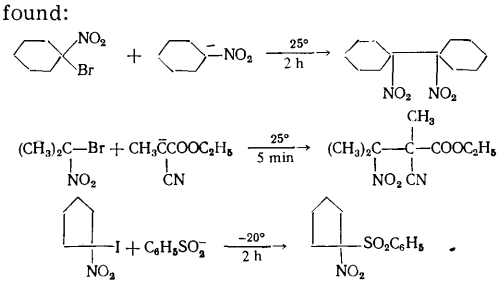
The mechanism of certain reactions between α-halogeno-α-nitro-compounds and nucleophiles, discovered previously, became understood in the light of these investigations. Thus, as early as 1940, Seigle and Hass[50] found that 2-halogeno-2-nitropropanes react with the sodium salt of 2-nitropropane to form 2,3-dimethyl-2,3-dinitrobutane:

$$(CH_3)_2C(NO_2)X + (CH_3)_2\bar{C}NO_2 \rightarrow (CH_3)_2C(NO_2)-C(NO_2)(CH_3)_2 ;$$
$$X = Cl, Br \text{ or } I.$$

The reaction between 2-chloro-2-nitropropane and sodioethylmalonic ester proceeds with a 68% yield[51]:

$$(CH_3)_2C(NO_2)Cl + C_2H_5\bar{C}(COOC_2H_5)_2 \rightarrow (CH_3)_2C(NO_2)-C(C_2H_5)(COOC_2H_5)_2 .$$

In recent years, mainly as a result of the efforts of Kornblum's[49,52] and Russell's[46] groups, new examples of the substitution of the halogen in α-halogen-α-nitro-derivatives via the radical-anionic chain mechanism have been found:



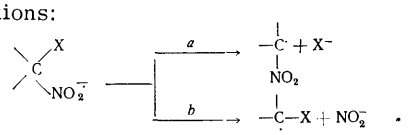
The reactions are catalysed by light and are inhibited by di-t-butylnitroxyl, *p*-dinitrobenzene, or triphenylmethyl radicals.

Reactions of this kind constitute the basis of the synthesis of α,β-unsaturated nitriles, ketones, and esters, where the first stage is the interaction of the sodium salts of $RCHYCOOC_2H_5$ (Y = CN, $COCH_3$, $COOC_2H_5$, or SO_2Ar) with α-halogeno-α-nitro-derivatives $R^1R^2CHalNO_2$ or the α,α-dinitro-derivatives $R^1R^2C(NO_2)_2$ in HMPA or DMF; subsequent heating of $R^1R^2C(NO_2)-CRYCOOC_2H_5$ in HMPA at 120°C leads to the formation of $R^1R^2C=CRY$;[53,54] the reduction of $R^1R^2C(NO_2)-CR(SO_2Ar)COOC_2H_5$ with sodium sulphide in DMF at room temperature yields $R^1R^2C=CRCOOC_2H_5$.[55]

Substitution of a sterically hindered nitro-group by hydrogen, including compounds synthesised via the $S_{RN}1$ mechanism, can be achieved by treatment with sodium methanethiolate in DMSO via the following mechanism[56]:

$$R_3C-NO_2 + CH_3S^- \rightarrow R_3C-NO_2^{\cdot-} + CH_3S^{\cdot} ;$$
$$R_3C-NO_2 \rightarrow R_3C^{\cdot} + NO_2^- ;$$
$$R_3C^{\cdot} + CH_3S^- \rightarrow R_3C-H + H_2\dot{C}-S^- ;$$
$$H_2\dot{C}-S^- + R_3C-NO_2 \rightarrow H_2C=S + R_3C-NO_2 .$$

Thus the decomposition of the intermediate radical-anions of the α-nitro-compounds can proceed, in principle, in two directions:



Pathway *a* obtains for X = Cl, Br, or I and pathway *b* obtains for X = COOR, COR, CN, or NO_2.

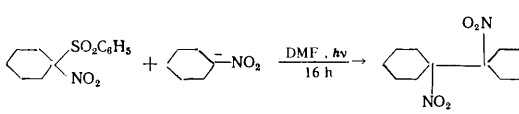
Owing to their instability the 2-nitropropane[57,58] and 2,2-dinitropropane[59] radical-anions are not revealed by EPR spectroscopy. The driving force of the decomposition of the radical-anions via pathway *a* is the presence of a readily eliminated group X and the formation of a resonance-stabilised nitroalkyl radical. The radical-anions derived from nitroalkanes[60] and α-fluoronitroalkanes[58] are fairly unstable but can be detected by EPR spectroscopy.

Yet another example of pathway *a* is provided by α-nitrosulphones. In the reaction of α-nitroisopropyl-*p*-tolyl sulphone with the potassium[61] or lithium[31] salts of 2-nitropropane in DMSO at 20°C the product was 2,3-dimethyl-2,3-dinitropropane in 80% (15 min) or 96% (2.5 h) yields:

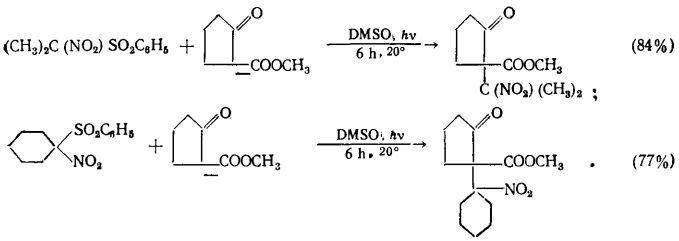
$$(CH_3)_2C(NO_2)SO_2C_6H_4CH_3\text{-}n + (CH_3)_2\bar{C}NO_2 \rightarrow (CH_3)_2C(NO_2)-C(NO_2)(CH_3)_2 .$$

Although the intermediate radical-anion of the initial sulphone was not detected in electrolysis in DMF or acetonitrile, all the results support the radical-anionic chain mechanism. The reaction is slower in the dark; when 5% of *p*-DNB is added it takes place to an extent of only 7% in 15 min, while in the presence of 5 mole % of di-t-butyl nitroxide its extent is only 1% after 4 h.

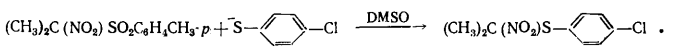
The reactions of α-nitrosulphones with other anions have also been studied[31]:



$$(CH_3)_2C(NO_2)SO_2C_6H_4CH_3\text{-}p + CH_3\bar{C}(COOC_2H_5)_2 \xrightarrow[2\ h]{DMSO,\ h\nu} (CH_3)_2C(NO_2)-C(CH_3)(COOC_2H_5)_2 ; \quad (82\%)$$



The reaction between α-nitroisopropyl-*p*-tolyl sulphone and the *p*-chlorothiophenoxide ion does not occur in the dark (DMSO, 2 h); under illumination by two 20-watt fluorescent lamps during the same period, the extent of the reaction is 95% and the corresponding sulphide is formed in 59% yield:



After 6 min, the extent of the reaction is 54%, while after the addition of 10 mole % of *m*-DNB it is only 13%; di-t-butylnitroxyl fully inhibits the reaction.

When α-nitroisopropyl phenyl sulphone is treated with six equivalents of sodium toluene-*p*-sulphinate in HMPA in the dark (20°C, 22 h) the reaction is not observed, while under illumination 25% of α-nitroisopropyl-*p*-tolyl sulphone is formed; the reaction is inhibited by the addition of 5 mole % of di-t-butylnitroxyl. The reverse reaction exhibits the same features:

$$(CH_3)_2C(NO_2)SO_2C_6H_5 + p\text{-}CH_3C_6H_4SO_2^- \rightleftarrows$$
$$\rightleftarrows (CH_3)_2C(NO_2)SO_2C_6H_4CH_3\text{-}p + C_6H_5SO_2^- \quad .$$

For the perfluoroalkylation of thiophenols [62,63], selenophenols [64], and sulphinic acids [65] by perfluoroalkyl iodides under illumination with ultraviolet light in liquid ammonia in accordance with the scheme:

$$ArXH + R_FI \xrightarrow[\text{liq. } NH_3]{h\nu} ArXR_F \ (X=S, Se, SO_2)$$

the authors propose the following radical-anionic chain mechanism:

$$ArS^- + R_FI \xrightarrow{h\nu} ArS^{\cdot} + R_FI^{\cdot -} \ ;$$
$$R_FI^{\cdot -} \rightarrow R_F^{\cdot} + I^- \ ;$$
$$ArS^- + R_F^{\cdot} \rightarrow [ArSR_F]^{\cdot -} \ ;$$
$$[ArSR_F]^{\cdot -} + R_FI \rightarrow ArSR_F + R_FI^{\cdot -} \ .$$

III. $S_{RN}1$ NUCLEOPHILIC SUBSTITUTION IN AROMATIC COMPOUNDS

Nucleophilic substitution in non-activated halogenobenzenes is known to proceed with much difficulty (if it occurs at all). The substitution of the halogen with a high yield can be achieved only in isolated reactions, for example, under the influence of lithium cuprates [66].

However, Bunnett and coworkers [67] showed that nucleophilic substitution in aryl halides or other aromatic compounds containing a group suitable for nucleophilic substitution can be readily achieved when metallic potassium (or sodium), which is an electron donor, is used as the catalyst, or under the influence of light. Naturally, activation by a metal in liquid ammonia is due to the solvated electron [68]. The amide ion, the thiophenoxide ion, carbanions such as the fluorenyl and cyanomethyl anions, and ketone enolates such as the acetonyl anion can function as nucleophiles [67].

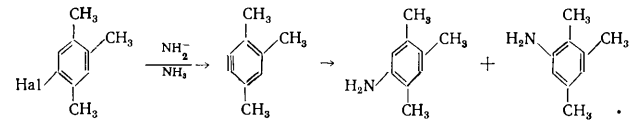
A different mechanism was proposed for these reactions: the substrate is reduced with formation of the aryl radical, which can interact subsequently with the nucleophile (anion), forming a radical-anion; the latter gives up an electron to the initial molecule and is converted into the reaction product [5]:

$$ArX + e \rightarrow [ArX]^{\cdot -} \text{ (chain initiation)}$$
$$\left.\begin{array}{l} [ArX]^{\cdot -} \rightarrow Ar^{\cdot} + X^- \\ Ar^{\cdot} + Y^- \rightarrow [ArY]^{\cdot -} \\ [ArY]^{\cdot -} + ArX \rightarrow [ArX]^{\cdot -} + ArY \end{array}\right\} \text{ (chain propagation)}$$
$$Ar^{\cdot} + RH \rightarrow ArH + R^{\cdot} \quad \text{(chain termination).}$$

Thus the new mechanism is based on the possibility of generating aryl radicals from ArX and on the hypothesis that a reaction takes place between Ar· and the anion. In other words, it is suggested that the anion behaves as "trap" for the aryl radical.

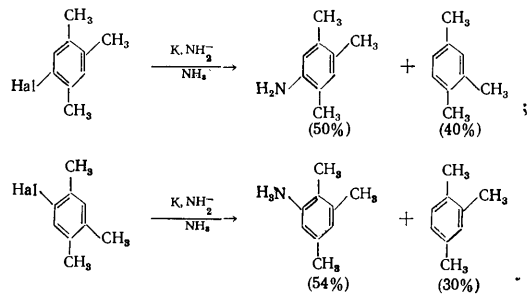
Liquid ammonia is usually employed as the solvent. The results depend on the experimental conditions, for example, on the way in which the carbanions are formed—by the action of KNH_2 or metallic potassium (whether or not the system contains an excess of electrons capable of reducing the aryl radical to the anion, i.e. $Ar^{\cdot} \rightarrow Ar^-$, depends on this). However, in most cases it is possible to select conditions ensuring a high yield of the nucleophilic substitution product.

The $S_{RN}1$ mechanism for reactions involving aromatic compounds was postulated for the first time in order to account for the results of the reaction of aryl halides (Hal = Cl, Br, or I) with the amide ion in liquid ammonia [5,69]. This reaction, involving 5- or 6-halogenopseudocumenes, proceeds via the aryne mechanism and leads to a mixture of isomers, whose composition is independent of the nature of the halogen for Hal = Cl or Br:

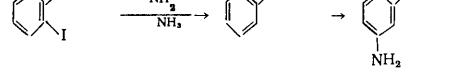


In the case of the more readily reducible ArI this mechanism is accompanied by another substitution reaction pathway, which leads to a different ratio of the isomers.

In the presence of metallic potassium, the aryne mechanism is suppressed, and the substitution proceeds wholly at the carbon atom linked to the halogen [69]:



o-Anisidine was obtained in 68% yield from *o*-iodoanisole, together with *m*-anisidine (17%) and anisole (8%). [69] The formation of *m*-anisidine is characteristic of the aryne mechanism:



The products of the substitution of the halogen for hydrogen (anisole or pseudocumene) are probably formed in the chain termination stage owing to the interaction of the aryl radical with the solvent.

In the presence of potassium reactions take place in the complete absence of the catalyst; thus iodobenzene reacts with potassium amide to form diphenylamine (19%) and *o*- and *p*-aminobiphenyls (11% of each)[69]. In acetonitrile, in the presence of potassium, chlorobenzene reacts with the cyanomethyl ion to form benzyl cyanide (36%) as well as benzene (26%) and toluene (18%). The latter might have been formed as a result of the decomposition of the radical-anion:

$$[C_6H_5CH_2CN]^{\cdot-} \rightarrow CN^- + C_6H_5\dot{C}H_2 \xrightarrow{RH} C_6H_5CH_3 .$$

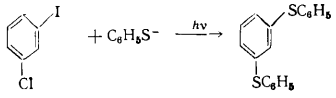
Subsequently it was shown that the $S_{RN}1$ reactions are initiated also by radiation. Under these conditions, aryl iodides react with the anion Ar'S' with formation of asymmetric sulphides in 70–95% yield[70]:

$$ArI + e \xrightarrow{h\nu} [ArI]^{\cdot-} ;$$
$$[ArI]^{\cdot-} \rightarrow Ar^{\cdot} + I^- ;$$
$$Ar^{\cdot} + Ar'S^- \rightarrow [ArSAr']^{\cdot-} ;$$
$$[ArSAr']^{\cdot-} + ArI \rightarrow [ArI]^{\cdot-} + ArSAr' .$$

The reaction constitutes a convenient method for the synthesis of diaryl sulphide, since for its occurrence it is sufficient to irradiate a solution of the reactants in liquid ammonia with light having $\lambda_{max} = 350$ nm. It has been noted that bromobenzene reacts much more slowly than iodobenzene. The absence of symmetrical sulphides from the reaction mixture implies that electron transfer is faster than the fragmentation of the radical-anion $[ArSAr']^{\cdot-}$ into an aryl radical and an arenethiolate anion. This conclusion is confirmed by the formation of the same sulphide (in 73–76% yield) in reactions of *p*-iodoanisole with $C_6H_5S^-$ and of iodobenzene with *p*-$CH_3OC_6H_4S^-$.[71]

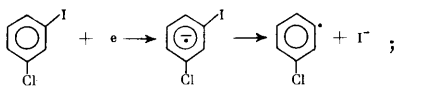
However, the problem of the mechanism of the initiation stage still remains open; it is not clear whether irradiation promotes electron transfer from the anion to the aromatic substrate or whether the C–X bond undergoes homolysis under the influence of radiation. The first version appears more probable, although in the case of iodobenzene one cannot rule out the possibility that the activation in certain reactions proceeds as a result of the photolysis of the C–I bond.

When the *m*-dihalogeno-derivative is introduced into the reaction with $C_6H_5S^-$, then, apart from fluoro-derivatives, the product of the substitution of both halogens—di(thiophenoxy)benzene[72] (only traces of the monosubstituted compounds are obtained)—is formed in a high yield in all cases:

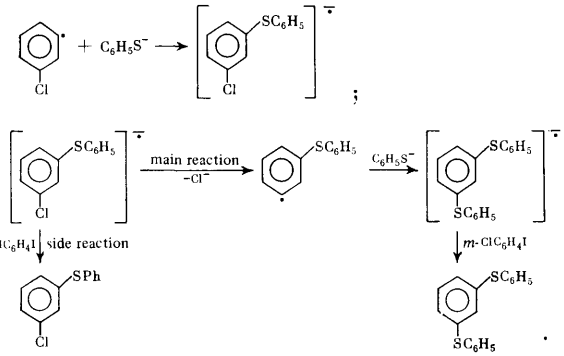


(91%)

The reaction of *m*-fluoroiodobenzene results in the formation of *m*-$FC_6H_4SC_6H_5$ (96%) only. The authors[72] believe that this result confirms the mechanism in which the rate of fragmentation of the radical-anion $[m\text{-}ClC_6H_4SC_6H_5]^{\cdot-}$ is higher than that of electron transfer:



;



Naturally, the only exception should be the radical-anion $[m\text{-}FC_6H_4SC_6H_5]^{\cdot-}$, since the carbon–fluorine bond is ruptured with difficulty and electron transfer predominates.

The photostimulated reaction with $C_2H_5S^-$ is much slower than that with ArS^-:

$$C_6H_5I + C_2H_5S^- \xrightarrow[NH_3]{h\nu} \underset{(30\%)}{C_6H_5SC_2H_5} + \underset{(44\%)}{C_6H_5S^-} + \underset{(3\%)}{(C_6H_5)_2S} .$$

The composition of the products of this reaction shows that radical-anion $[C_6H_5SC_2H_5]^{\cdot-}$ only partly gives up its electron to iodobenzene; most of it is able to fragment with formation of $C_2H_5^{\cdot}$ and $C_5H_5S^-$. Precisely this fragmentation pathway is observed in reduction with ArSAlk. The $C_6H_5S^-$ formed can interact with iodobenzene to give diphenyl sulphide (via the same $S_{RN}1$ mechanism).

Together with the C–N and C–S bonds, photostimulated aromatic nucleophilic substitution makes it possible to obtain the C–P bond. Thus the reactions of various aryl iodides with potassium dialkyl phosphites lead to the formation of arylphosphonates in a high yield (87–96%):[73, 74]

$$(RO)_2POK + ArI \xrightarrow[NH_3]{h\nu} ArP\underset{\underset{O}{\|}}{(OR)_2} .$$

1-Iodonaphthalene is converted after 2 h into the corresponding phosphonate in 93% yield (4% in the absence of radiation)[73]. The radical-anion of the aryl halide and the dialkyl phosphite radical are formed initially:

$$ArX + (RO)_2PO^- \xrightarrow[NH_3]{h\nu} [ArX]^{\cdot-} + (RO)_2PO^{\cdot} .$$

Next the reaction proceeds via the usual pathway involving the formation of $[ArPO(OR)_2]^{\cdot-}$. It is suggested that this radical-anion is more stable than $[ArSAr]^{\cdot-}$ owing to the more pronounced electron-accepting properties of the $OP(OR)_2$ group and for this reason it interacts with aryl halide instead of decomposing.

The ratio of the products of mono- and di-substitution was investigated as a function of the nature of the halogen in a series of studies on the substitution of halogens under the influence of $(RO)_2PO^-$ in dihalogenobenzenes under irradiation[75–77]. The authors of these studies state that the results agree solely with the $S_{RN}1$ mechanism.

The possibility of employing this reaction for the synthesis of aryl phenyl selenides in high yields has been demonstrated:

$$ArX + C_6H_5Se^- \xrightarrow[liq.\ NH_3]{h\nu} ArSeC_6H_5 .$$

This reaction proceeds only with halogeno-derivatives of phenanthrene, naphthalene, and biphenyl, but not benzene[78].

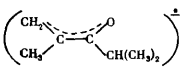
The new reaction involving the arylation of nucleophiles can be used to form carbon–carbon bonds. After initiation by an alkali metal or irradiation, various carbanions,

including ketone enolates, are arylated under the influence of ArX. Thus it has been shown that bromobenzene does not react with the potassium enolate of acetone in the dark, but, under illumination with near ultraviolet light (150 W), phenylacetone is formed in a high yield [79] with a small admixture of 1,1-diphenyl-2-propanone—the double phenylation product. In contrast to bromobenzene, iodobenzene undergoes this reaction also in the dark, but under irradiation it is appreciably accelerated (5–15% of the product is formed in the dark after 3 h, while the yield under irradiation is 67%). 3-Pentanone and 4-heptanone are phenylated in the α-position in 80% yield [80]. The radical chain mechanism is confirmed by the inhibiting effect of radical traps of the type of di-t-butylnitroxyl and also oxygen. Although the yield of the ketone phenylation products does not in general exceed the yields obtained by other methods (for example, in the phenylation of enolates by means of iodonium salts [81]), the proposed reaction is preparatively more convenient.

In the presence of sodium or potassium the reactions of aryl halides with acetone enolate give rise to a mixture of the ketone $ArCH_2COCH_3$ and the alcohol $ArCH_2CH(OH).CH_3$, with an overall yield up to 89%, as well as a certain amount of 1,1-diarylacetone [82]. Since the ketone is not reduced to the alcohol under these conditions but forms a ketyl, it is suggested that the radical-anion $[ArCH_2.COCH_3]^{\cdot-}$ is reduced and that this reaction proceeds simultaneously with its "oxidation" under the influence of ArX.

Bromo- and iodo-benzenes react similarly with the enolate ion derived from 2-butanone and 3-methyl-2-butanone [83]. Regardless of the method of initiation (by potassium or by illumination with light), 2-butanone gives rise to a mixture of phenylated ketones—$C_6H_5CH_2COCH_2.CH_3$ and $CH_3COCH(C_6H_5)CH_3$; the reaction of 3-methyl-2-butanone also results in a mixture of isomers, but the isomer $C_6H_5CH_2COCH(CH_3)_2$ predominates (81% yield).

When enolate ions derived from ketones such as di-isopropyl ketone are used as the anion in a photostimulated reaction with iodobenzene, benzene and a dimeric product (A) are formed together with the ketone arylation product. It is suggested that, apart from the usual reaction involving the radical-anion formed, the phenyl radical abstracts a β-hydrogen atom from the radical-anion. Since the radical-anion



formed is fairly stable, it is not involved in electron transfer, but is stabilised with formation of (A) or disproportionates to form a dianion and an unsaturated ketone [84]:

$$(CH_3)_2-\underset{\underset{O}{\|}}{C}-C(CH_3)_2-CH_2-C(CH_3)_2-\underset{\underset{O}{\|}}{C}-C(CH_3)_2 \quad (A)$$

The $S_{RN}1$ mechanism has also been resorted to in order to account for the causes of the formation of the dimeric product

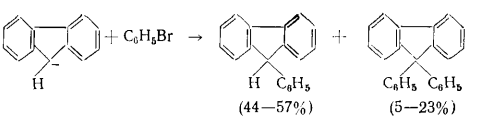
$$(C_6H_5)_2C(CONR_2)-C_6H_4-C(C_6H_5)CONR_2$$

when 2-bromo-*N*,*N*-dimethyl-2-diphenylacetamide is acted upon by an excess of sodium methoxide in 2,2-dimethoxypropane [85].

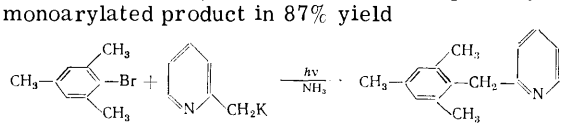
The arylation of cyclic ketones (cyclobutanone, cyclopentanone, cyclohexanone, cyclo-octanone, and 2-indanone), initiated by radiation, takes place with excellent yields [80]. However, it has been shown in the same study that the reaction is not undergone by the monoanions of β-dicarbonyl compounds, although as can be seen from the first part of the review, alkyl radicals do react with these anions. It is suggested that arylation in such cases involves ready chain termination, although the true cause has not yet been established.

The influence of the nature of Ar in ArX on the yield of the product $ArCH_2COCH_3$ has been studied in relation to the photochemically initiated arylation of the acetone enolate ion [86]. The reactions of $2,4-(CH_3O)_2C_6H_3Br$, $2,4,6-(CH_3O)_3.C_6H_2I$, $2-\bar{O}OCC_6H_4Br$, and $2,5,6-(CH_3)_3C_6H_2I$ take place with with satisfactory yields. The reactions of compounds in which the benzene ring contains several bulky alkyl substituents take place much less effectively. After 1.5 h, the compounds $4-(C_2H_5)_2NC_6H_4Br$, $4-\bar{O}C_6H_4Br$, and $3-NO_2C_6.H_4Br$, i.e. compounds with any strong electron-donating or electron-accepting substituents, altogether failed to give an arylation product. 1- and 2-Iodonaphthalenes, 9-bromoanthracene, and 9-bromophenanthrene proved to be effective arylating agents.

The possibility of arylating "purely carbon" carbanions has also been demonstrated [86]. For example, the anion of penta-1,3-diene reacts with bromobenzene in the presence of potassium (NH_3, $-78°C$) to give a mixture of phenylated mono- and di-olefins. 3-Phenylindene (32%), 1-phenylindene (3%), diphenylindene (11%), and triphenylindene (4%) were obtained by the reaction of the indene anion with bromobenzene. The fluorene anion reacts similarly in the presence of potassium or sodium:



In those cases where the reaction of the carbanion with ArX proceeds also without a catalyst, for example, the interaction of α- and γ-picolinyl anions with bromo- or iodo-benzene [83], the yield can be increased by adding potassium or by irradiation. For example, the yield in the reaction with bromobenzene is 57% in the dark and 73% under irradiation, while the yield in the reaction with iodobenzene alone is 14% and 63% in the presence of potassium (the overall yield of the products of mono- and di-arylation is indicated); on the other hand, the reaction with chlorobenzene does not take place at all without initiation. The aryne mechanism has been proposed for the dark reaction, which has been confirmed by the absence of arylation in the case of bromomesitylene; however, the $S_{RN}1$ process takes place readily under the influence of irradiation and leads to the formation, in the case of the α-picolinyl anion, of a monoarylated product in 87% yield



The phenylation of α-cyano-carbanions in the presence of potassium is more complex [5,87]. Thus chlorobenzene reacts with the cyanomethyl anion in the presence of potassium in liquid ammonia to form phenylacetonitrile, toluene, benzene, and aniline. Significant amounts of 1,2-diphenylethane were obtained in the analogous reaction with iodobenzene together with the product already enumerated. It is noteworthy that the process itself takes place readily, in contrast to the photochemical reaction,

‡ It has been shown specially that benzyl radicals do not interact with anions.

which takes place appreciably less effectively than the reaction with the acetone enolate ion:

$$C_6H_5X + \bar{C}H_2CN \rightarrow [C_6H_5X]^{\cdot-} + {}^{\cdot}CH_2CN \quad ;$$

$$[C_6H_5X]^{\cdot-} \rightarrow C_6H_5^{\cdot} + X^- \quad ;$$

$$C_6H_5^{\cdot} + \bar{C}H_2CN \rightarrow [C_6H_5CH_2CN]^{\cdot-} \quad ;$$

$$CN^- + {}^{\cdot}CH_2C_6H_5^{\bullet} \leftarrow [C_6H_5CH_2CN]^{\cdot-} \xrightarrow{C_6H_5X} [C_6H_5X]^{\cdot-} + C_6H_5CH_2CN \quad ;$$

$$\downarrow +e_s$$

$$C_6H_5\bar{C}H_2CH_2C_6H_5 \quad C_6H_5\bar{C}H_2 \xrightarrow{NH_3} C_6H_5CH_3 + NH_2^- \quad ;$$

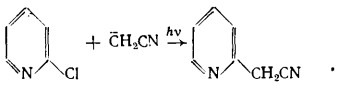
$$C_6H_5^{\cdot} + e_s \rightarrow C_6H_5^- \xrightarrow{NH_3} C_6H_6 + NH_2^- \quad ;$$

$$C_6H_5^{\cdot} + NH_2^- \rightarrow [C_6H_5NH_2]^{\cdot-} \xrightarrow{C_6H_5X} [C_6H_5X]^{\cdot-} + C_6H_5NH_2 \ .$$

The formation of all the products can be explained by a scheme postulating the ready interaction of $C_6H_5^{\cdot}$ with $\bar{C}H_2CN$ as well as the fragmentation of the resulting radical-anion. It is noteworthy that the elimination of the cyano-group from the benzyl cyanide formed can take place similarly under the influence of potassium [88]. The formation of hydrocarbons even in solvents from which the radical cannot abstract a hydrogen atom can be explained by the reduction of the radicals to the anions. Thus the reaction of $C_6H_5^{\cdot}$ with NH_3 is ruled out in view of the absence of benzene from the products of the reaction with acetone enolate ions, although the reaction was carried out in the presence of an effective hydrogen donor—the isopropoxide anion. The fraction of toluene and diphenylethane in the reaction product increases for fluorobenzene, which is reduced with difficulty under the influence of the radical-anion. The corresponding reaction with the anions obtained from other nitriles leads to the formation of different alkylbenzenes.

It has been shown recently [89] that, when a number of aryl halides other than C_6H_5X are used, the above reaction leads to the formation of α-aryl- or α-heteroaryl-acetonitriles in very satisfactory yields, and can therefore be of synthetic interest.

The arylation of the anion $\bar{C}H_2CN$ in liquid ammonia under irradiation, leading to $ArCH_2CN$ in nearly quantitative yields, has been achieved for 1- and 2-chloronaphthalene, 4-chlorobiphenyl, 4-bromobenzophenone, and 2-chloropyridine, for example:



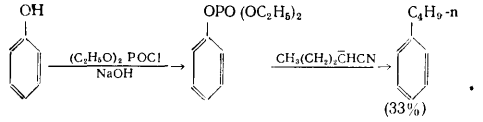
(98%)

9-Bromophenanthrene reacts similarly (the yield of the arylation product is 60–70%). It is of interest to note that the reactivity of the anion $\bar{C}H_2CN$ in these reactions is approximately the same as that of the acetone enolate, i.e. the differences between the rates of these reactions with bromobenzene are determined by other stages.

The results were explained by examining the distribution of electrons in the resulting radical-anion using the molecular orbital perturbation theory [99]. However, in practice we are dealing with the greater stability of the radical-anion $[ArCH_2CN]^{\cdot-}$ compared with $[C_6H_5CH_2N]^{\cdot-}$.

It is of interest that, together with halogeno-derivatives of aromatic compounds, other aromatic compounds, containing groups capable of being fairly readily eliminated as anions, can be used in this reaction [91]. Thus $ArSC_6H_5$ (but not $C_6H_5SC_2H_5$) reacts under the influence of irradiation with the acetone enolate ion to form $ArCH_2COCH_3$, but the extent of the fragmentation of the radical-anion can be very great, depending on the nature of Ar. The relative contributions of the processes can be inferred from the ratio of the yields of the two ketones $C_6H_5CH_2COCH_3$ and $ArCH_2COCH_3$. An approximate estimate of the reactivities of ArX gives the following sequence: $I \simeq Br > SC_6H_5 \gg Cl > F \gg OC_6H_5$. [71,79] The sulphonium and ammonium salts $(C_6H_5)_3^{\bullet}SCl^-$ and $C_6H_5^{\bullet}N(CH_3)_3I^-$ are fairly reactive. Thus the reaction of $C_6H_5^{\bullet}N(CH_3)_3I^-$ with the α-picolinyl anion leads to the arylation products in 88% yield (3% of the diarylated derivative is also formed) [92].

In some cases the $OPO(OC_2H_5)_2$ group proved to be particularly convenient for preparative purposes. The corresponding ester can be obtained in a high yield (87%) from phenol under the influence of $(C_2H_5O)_2POCL$ in the presence of alkali. Treatment of the resulting ester with, for example, the anion $CH_3(CH_2)_2\bar{C}HCN$ leads to n-butylbenzene in 38% yield. Thus the overall yield in this process is 33%; this reaction is of synthetic value, because it makes it possible to introduce an alkyl group into a specific position in the benzene ring and, in contrast to the Friedel–Crafts reaction, only the non-rearranged product can be obtained. Furthermore, in those cases where a nitrile is formed in the reaction, the cyano-group can be readily removed from the latter with formation of the same alkyl derivative:



The use of a phosphate ester for the conversion of phenols into anilines is of particular interest [93]. The yield of anilines in the reaction of aryl diethyl phosphate with potassium amide in liquid ammonia in the presence of potassium is 56–78%:

$$ArOPO(OC_2H_5)_2 + KNH_2 \xrightarrow[NH_3]{K} ArNH_2 \ .$$

(Ar = phenyl, 2,6-dimethylphenyl, or 2-methoxy-4-methylphenyl).

The $S_{RN}1$ mechanism has been proposed for the non-catalysed reaction of arenediazonium salts $ArN_2^{\bullet}X^-$ with potassium iodide in methanol [94,95], whose products are ArI, ArH, and formaldehyde. It is suggested that the first stage involves the reduction of the diazonium cation by the iodide ion with formation of $[ArN_2]^{\cdot}$, which decomposes to Ar$^{\cdot}$ (or R–⟨⊙⟩–⊕). The radical interacts with the iodide ion to form $ArI^{\cdot-}$, which reduces the initial cation.

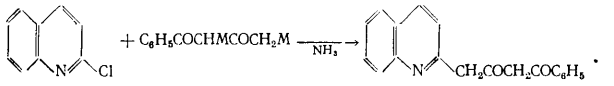
It has been shown that DMSO can be used successfully in the $S_{RN}1$ reaction instead of ammonia [96–98]. The reactions of iodobenzene with diethyl phosphite, the thiophenoxide ion, and ketone enolate ions have been achieved in this solvent in high yields under the influence of irradiation. It is of interest that in the last case the $S_{RN}1$ process can be thermally induced. However, the authors [92,98] note difficulties in the interpretation of the kinetics observed in DMSO. The dimsyl ion is phenylated with high yields in DMSO under the influence of bromobenzene (80%) and iodobenzene (87%). [99] The authors of this study, who live in Madras, note that under their climatic conditions the reaction takes place simply under the influence of sunlight. An important advantage of DMSO compared with other solvents is its low reactivity as a donor of hydrogen atoms compared with phenyl radicals, although the reaction products can be more conveniently isolated from ammonia. Other promising solvents are DMF and acetonitrile, where the reaction of iodobenzene with $(C_2H_5O)_2POK$ has been shown to take place with high yields [96].

The possibility of $S_{RN}1$ processes in 50% aqueous t-butyl alcohol has been demonstrated in relation to the reaction of C_6H_5X (X = Cl, Br, or I) with sodium phenoxide catalysed by sodium amalgam [100]. The reaction leads to the formation of diphenyl ether and benzene, the former being the main product of the reaction with iodobenzene and the latter that of the reaction with chlorobenzene, which can be accounted for by the different rates of reduction of these halogenobenzenes. It is suggested that in the reaction with C_6H_5Cl, phenyl radicals are formed at a low rate but are able to diffuse into the solution and are reduced on the surface of the amalgam to anions. In conformity with the $S_{RN}1$ mechanism, the reaction does not occur in the absence of Na/Hg and is inhibited by oxygen.

Extremely fruitful results were obtained by carrying out $S_{RN}1$ reactions as well as other anionic processes under the conditions of interfacial catalysis [101-103]. Norris and coworkers [101] showed that, under these conditions, which make it possible to reduce the amount of the aprotic dipolar solvent, the reactions of nitroalkane anions take place with *p*- or *o*-nitro-substituted benzyl or benzylidene chlorides and also with *p*-dinitrobenzene to given excellent yields of products. 2-Nitro-2-(*p*-nitrophenyl)propane is formed in the reaction of the tetrabutylammonium salt of 2-nitropropane with *p*-dinitrobenzene in acetone or benzene in yields up to 76% after only 5 min, i.e. much faster than in the usual procedure in DMSO. [101,104]

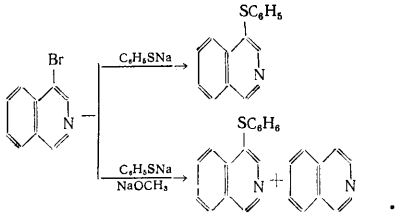
It has been shown recently for reactions of halogeno-derivatives of naphthalene, benzophenone, and benzonitrile with the thiophenoxide ion that substitution via the $S_{RN}1$ mechanism can be initiated electrochemically [105].

The $S_{RN}1$ mechanism was postulated for the first time for nucleophilic substitution in heterocyclic compounds in the reaction of the benzoylacetone dianion with 2-chloroquinoline [106]:



Since the reaction occurred without irradiation and in the absence of an alkali metal, the authors suggested that the reduction proceeds under the influence of the ambident anion itself. The radical chain mechanism was indicated by the powerful influence of inhibitors of the type of *p*-dinitrobenzene. The same workers showed that the interaction of 2-chloroquinoline with $LiCH_2COR$ (R = CH_3 or C_6H_5) in liquid ammonia (−33 °C) is sharply accelerated on irradiation with near ultraviolet light or in the presence of a small amount of added $C_6H_5COCH(Li)COCH_2Li$. [107] The reactions of potassium enolates of various ketones take place readily under the influence of irradiation; the ketone $R^1R^2CHCOCH_3$ then reacts not only with the primary but also with the tertiary carbon atom [108]. Under these conditions, 2-chloroquinoline exhibits a higher reactivity than iodobenzene. It is of interest that, as in the case of halogenobenzenes, the reaction does not take place with the monoanions of β-dicarbonyl compounds. The authors postulate the $S_{RN}1$ mechanism [109] for the reaction of 3-bromoquinoline with the superoxide ion, because bromine in the 3-position is usually relatively unreactive in nucleophilic aromatic substitution reactions.

4-Phenylthioisoquinoline is formed in the reaction of 4-bromoisoquinoline with sodium thiophenoxide in methanol via the usual ionic mechanism (addition-elimination). However, it has been shown [110,111] that in the presence of sodium methoxide the reaction mechanism changes to a radical chain mechanism, which leads to the formation of a reduction product (isoquinoline) together with the substitution product; according to the authors, isoquinoline is formed as a result of the interaction of Ar· with the solvent:



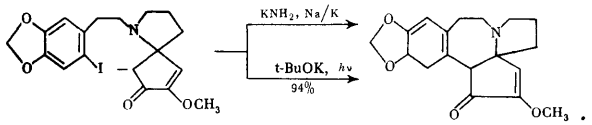
The remaining step is to postulate that, in contrast to the thiophenoxide ion, the methoxide ion behaves as an electron donor in this reaction. The possibility of the reduction of aryl halides under the influence of the methoxide ions is known. Thus it has been shown [111] that, in solution in CH_3OH-CH_3ONa (165 °C), 3-iodopyridine and 4-bromoquinoline give rise mainly to reductive dehalogenation products. The reaction proceeds via radicals, since deuterium is scarcely incorporated in the reaction product when CH_3OD is used. Although this is in fact a radical chain process, it does not have the $S_{RN}1$ mechanism, since there is no stage involving the addition of the anion to the radical. On the other hand, chain propagation proceeds in accordance with the following scheme:

$$CH_3O^- + ArX \rightarrow CH_3O^{\cdot} + ArX^{\cdot -} ;$$
$$ArX^{\cdot -} \rightarrow Ar^{\cdot} + X^- ;$$
$$Ar^{\cdot} + CH_3OH \rightarrow ArH + {}^{\cdot}CH_2OH ;$$
$$^{\cdot}CH_2OH + CH_3O^- \rightarrow CH_2O^{\cdot -} + CH_3OH ;$$
$$Ar^{\cdot} + CH_3O^- \rightarrow ArH + CH_2O^{\cdot -} ;$$
$$ArX + {}^{\cdot -}CH_2O \rightarrow ArX^{\cdot -} + CH_2{=}O .$$

It has been shown recently that, under the classical conditions of the $S_{RN}1$ reaction (ammonia, irradiation), 2-bromo-, 3-bromo-, and 2,6-dibromo-pyridines readily interact with potassium enolates derived from ketones; thus 2-acetonylpyridine is obtained after 15 min in 95% yield [112]. It has been noted that promotion with a metal in the case of heteroaromatic compounds is much less successful than in the case of carboaromatic systems.

The substitution of the halogen in 2- and 3-halogeno-thiophens under the influence of the acetone enolate ion and the amide ion has been achieved in both versions, i.e. under the influence of sodium and irradiation [113].

The $S_{RN}1$ reaction has found a remarkable application in intramolecular cyclisation with formation of the cyclic system of cephalotaxine—the starting material for the synthesis of the anticancer antibiotic cephalotazinone [114, 115]—and also in other similar cyclic systems [116]:



After the addition of the base and the formation of the carbonium ion, the reaction is initiated by an alkali metal or irradiation.

IV. $S_{RN}1$ NUCLEOPHILIC SUBSTITUTION AT AN OLEFINIC CARBON ATOM

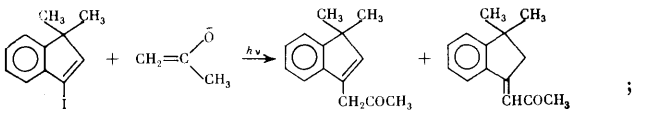
In 1976 the $S_{RN}1$ mechanism was extended to the reaction of vinyl halides [117]. It was found that β-bromostyrene reacts with potassium enolate of acetone under

irradiation (λ = 350 nm, 5 h) to form two isomeric unsaturated ketones (overall yield 82%) and a small amount of styrene (7%):

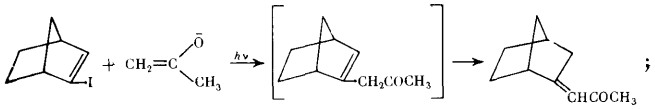
$$C_6H_5CH{=}CHBr + \bar{C}H_2COCH_3 \xrightarrow{h\nu,\,1} \underset{(48\%)}{C_6H_5CH{=}CHCH_2COCH_3} + \underset{(34\%)}{C_6H_5CH_2CH{=}CHCOCH_3} .$$

The reaction, initiated by metallic potassium, is accompanied by reduction, the saturated ketone $C_6H_5CH_2CH_2CH_2.COCH_3$ (63%) and the alcohol $C_6H_5(CH_2)_3CH(OH)CH_3$ (15%) being obtained.

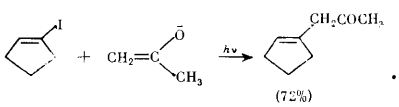
The reactions with 1-iodo-3-dimethylindene§, 2-iodonorborn-2-ene, and 1-iodocyclopentene[117] take place similarly:



;

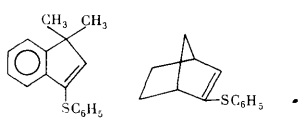


;



.

The reaction of the first two compounds with $C_6H_5S^-NH_4^+$ is slow, but also leads to substitution products:



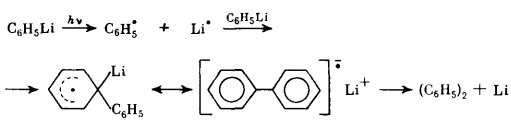
.

It is noteworthy that the authors do not regard the $S_{RN}1$ mechanism as rigorously proved in the reaction described.

V. GENERAL CONSIDERATIONS CONCERNING THE MECHANISM

The usual reactions of radicals are known to involve dimerisation, disproportionation, or the abstraction of an atom, usually a hydrogen atom, from the solvent[118,119]. The $S_{RN}1$ mechanism under consideration postulates that under certain conditions the radical can interact with the anion to form a radical-anion. There exist data confirming the possibility of this type of radical reaction.

The hypothesis that the phenyl radical adds to the phenyl anion was put forward to account for the formation of biphenyl in the photolysis of phenyl-lithium in ethereal solution[120]:



.

The direct detection of the radical-anions formed is of greatest interest. Such data have been obtained, although their number is extremely small. Thus it has been shown by EPR that certain aryl radicals (obtained by the reduction of ArN_2^+ under the influence of Ti^{3+}) add to the nitrite ion in aqueous solution with formation of radical-anions[133]. The occurrence of this stage demonstrates the reality of the subsequent chain mechanism of the substitution of the diazonium group by a nitro-group via the Sandmeyer reaction:

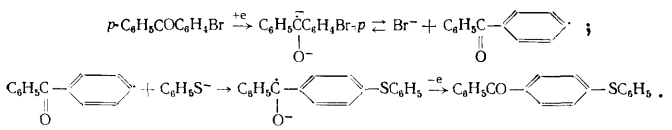
$$ArN_2^+ + Cu \rightarrow Ar^\cdot + N_2 + Cu^+ \ ;$$
$$Ar^\cdot + NO_2^- \rightarrow [ArNO_2]^{-\cdot} \ ;$$
$$[ArNO_2]^{-\cdot} + Cu^+ \rightarrow ArNO_2 + Cu \ .$$

The addition of the nitrophenyl radical to the iodide ion has been reported[123], but, according to other data[112], the radical-anion formed readily dissociates into the initial components. The radical-anions are not formed by the reaction with chloride and bromide ions[123].

Another example involves the interaction of the cyanide ion with the *p*-nitrophenyl radical, which is generated by the electrochemical reduction of *p*-iodonitrobenzene in DMSO.[123] The formation of the *p*-nitrobenzonitrile radical-anion (in a yield greater than 90%) was established by cyclic volt-amperometric and EPR methods:

$$p\text{-}NO_2C_6H_4^\cdot + CN^- \rightarrow [p\text{-}NO_2C_6H_4CN]^{-\cdot} \ .$$

Analogous radical-anions have been obtained from *o*- and *m*-nitrophenyl radicals. The reaction of $NO_2C_6H_4^\cdot$ with $C_6H_5S^-$ could not be investigated by these methods owing to the rapid interaction of $NO_2C_6H_4I$ with $C_6H_5S^-$. However, the hypothesis of the possible addition of the phenyl radical to the thiophenoxide anion was confirmed in a study[124] of the electrochemical reduction of *p*-bromobenzophenone in the presence of $C_6H_5S^-$; as a result of the oxidation-reduction cycle, the authors obtained the nucleophilic substitution product[124]:



.

However, it has been shown recently[125] that the product of this reaction may be formed by the usual $S_{RN}1$ mechanism in which the initial compound abstracts an electron from the radical anion; the only difference is that in the given instance the electron in the radical-anion is localised in the side chain and not in the aromatic ring.

The problem of the structure of the radical-anion obtained by the interaction of aryl radicals with the cyanomethyl anion has been considered in a study[90] using the method of the molecular orbital perturbation theory; the relative stabilities of the radical-anions were estimated as a function of the distribution of their electron density:

$$[Ar]^{-\cdot} CH_2Z \rightleftarrows ArCH_2 [Z]^{-\cdot} \ .$$

The hypothesis that the alkyl radical can interact with the nitrite ion to form a radical-anion was put forward by the authors of a monograph[119] to account for experimental data[126] having observed that *gem*.-dinitro-compounds are formed in the electrolysis of aliphatic nitro-compound in an alkaline medium in the presence of nitrite ions.

Thus the possibility of a stage involving the addition of the radical to the anion in the $S_{RN}1$ mechanism gives rise to no doubts.

Another fundamental problem arising when the $S_{RN}1$ mechanism is considered concerns the source of electrons This applies particularly to reactions where no catalyst is introduced and to processes initiated by irradiation. When metallic potassium is introduced into the reaction, there

§ The reaction does not take place in the dark even in the presence of an excess of the enolate.

is no doubt about the possibility of the formation of $[ArX]^{\cdot-}$, since it is known that all aryl halides are capable of being reduced by the solvated electron or electrochemically[127]. In principle, it is possible to envisage the reduction of ArX under the influence of certain anions (or nucleophiles). Thus a one-electron transfer stage has been observed for certain nucleophilic substitution reactions using a fairly readily reducible substrate. For example, the reactions of iodonitrobenzenes (but not the chloro- and bromo-derivatives) with bulky amines give rise to a nitrobenzene together with substitution products and sometimes as the main product, i.e. reductive dehalogenation via a radical mechanism takes place[128]. Analogous reduction processes under the influence of CH_3O^- [110,111] were examined above.

However, the problem remains how irradiation promotes this process. In some instances one cannot rule out the possibility that irradiation leads to the rupture of the Ar–X bond, particularly in the case of aryl iodides[129-131]. The possibility of this reaction pathway (together with the photostimulated electron transfer) was rejected by Bunnett and coworkers[80], because the reactivities of bromo- and iodo-benzenes differ insignificantly.

Hoz and Bunnett[132] recently made a detailed study of the reaction of iodobenzene with the diethyl phosphite ion initiated by irradiation. They showed that the reaction is preceded by the formation of a charge-transfer complex. It was found that the reaction is inhibited by nitroxy-radicals but is insensitive to the presence of oxygen and copper chloride. Kinetic measurements showed that the quantum yield of the reaction is greater than unity and that chain termination is a first-order process, which is confirmed by the virtually complete absence of biphenyl from the reaction products. On the basis of these results, the authors concluded that the radical-anion propagating the chain in the $S_{RN}1$ mechanism is formed by one of the following pathways:

$$\text{I (a) } PhI \overset{h\nu}{\rightleftarrows} (PhI)^*\ ,$$

$$(PhI)^* + (EtO)_2PO^- \rightarrow [PhPO(OEt)_2]^{\cdot-} + I^\cdot\ ;$$

$$\text{(b) } (PhI)^* + (EtO)_2PO^- \rightarrow Ph^\cdot + I^- + (EtO)_2PO^\cdot\ ;$$

$$Ph^\cdot + (EtO)_2PO^- \rightarrow [PhPO(OEt)_2]^{\cdot-}\ ;$$

$$\text{II } PhI + (EtO)_2PO^- \rightleftarrows PhI\cdot(EtO)_2PO^-\ ;$$

$$PhI\cdot(EtO)_2PO^- \overset{h\nu}{\rightarrow} [Ph\cdot I^-\cdot OP(OEt)_2]^* \rightarrow PhPO(OEt)_2 + I^-\ ;$$

$$[Ph\cdot I^{\cdot-} OP(OEt)_2]^* + (EtO)_2PO^- \rightarrow [PhPO(OEt)_2]^{\cdot-} + I^- + (EtO)_2PO^\cdot\ .$$

Virtually no kinetic studies on the $S_{RN}1$ mechanism have been described in the literature hitherto. The first attempt at such an investigation was undertaken by Perez de Marquez et al.[133], who used a flow technique involving very rapid contact between a p-$XC_6H_4-C_6H_5$ solution (X = F, Cl, Br, or I) in a 2 : 1 tetrahydrofuran–dimethoxyethane mixture and the surface of a potassium mirror (at −135°C) and detected the radical-anion $[ArH]^{\cdot-}$ in the EPR spectrum. They showed that the rate of its disappearance in an excess of ArX is consistent with first-order kinetics. However, we believe that this study has no direct bearing on the $S_{RN}1$ mechanism.

It is quite evident that the new mechanism of nucleophilic substitution at the carbon atom under consideration is still in its formulation stage, and that its further development in both theoretical and practical respects will be achieved in the immediate future.

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Electrochemistry of Metal Chelates in Non-aqueous Media

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A systematic account is given of experimental data on the electrochemical coordination reactions of compounds of metals with organic ligands in non-aqueous media. Attention is concentrated on the results of polarographic studies on the so-called inert chelate complexes. The influence of the nature of the metal and the ligand on the mechanism of the electrode reaction is discussed.
The bibliography includes 100 references

CONTENTS

I. Introduction 449
II. Electrochemical reduction of metal chelates with organic ligands in non-aqueous media 449
III. Anodic reactions of metal coordination compounds 457
IV. The role of the nature of the metal and the structure of the ligand in the mechanism of the electrochemical reduction of chelates 459

I. INTRODUCTION

Interest in the electrochemistry of coordination compounds in non-aqueous solutions is due to a number of causes. On the one hand, the vigorous development of inorganic chemistry and in the first place the chemistry of complex compounds requires tests on fundamental relations by various methods, including electrochemical methods. On the other hand, progress in electrochemistry, both theoretical (development of the theory of kinetic currents, mechanisms involving chemical reactions accompanied by charge transfer) and experimental (new apparatus permitting the recording of polarisation curves in solutions with a high ohmic resistance, new procedures for the detection of short-lived species at the electrode, etc.), has also stimulated the study of complexes in non-aqueous media by electrochemical methods. Many chelates are insoluble in aqueous media and the use of non-aqueous solvents therefore ensures suitable conditions for their investigation. From the practical point of view, studies in this field permit the solution of problems of electrocatalysis, electroplating, electrosynthesis of organometallic complexes (catalysts), and finally electroanalytical determination of metals.

Advances achieved hitherto in the polarography of organic compounds in aqueous and aqueous-organic media permit a more detailed examination of the effects accompanying the reduction of a complex species combined with an organic ligand. Virtually all organic substances are adsorbed to some extent on the surface of the mercury dropping electrode (m.d.e.), so that the shift of the half-wave potential ($E_{1/2}$) and the change in the slope of the reduction wave for the metal ion in solution in the presence of the organic ligand, on which conclusions concerning the stability of the complexes in solution and their composition are based, can be induced not only by complex formation but also by the inhibition of the reduction at the electrode, a change in the ψ' potential, etc. These effects are observed mainly when the region corresponding to the reduction of metal ions coincides with the region of the maximum adsorption of the organic ligand.

The study of complex formation processes by polarographic methods in non-aqueous media or in aqueous organic media with a high content of an organic solvent, where adsorption is considerably weakened and the above effects do not complicate the electrochemical reactions of complexes, is also promising in this connection. Furthermore, under these conditions, there is virtually no hydrolysis in solutions. The low dielectric constants of the majority of organic solvents have a significant influence on the behaviour of complexes at the electrode. Many metal ions, forming stable complexes in aqueous media, are highly solvated in organic solvents (for example, in ethylenediamine, formamides, acetonitrile, and dimethyl sulphoxide) and are characterised by high donor numbers. Problems of the solvation of metal cations have been reviewed recently in a collection of reports on non-aqueous electrochemistry[1]. The conditions governing the selection of a suitable solvent, supporting electrolyte, and reference electrode for the investigation of chelates are also discussed there.

Attention has been particularly concentrated recently on the use of aprotic solvents, for example, dimethylformamide (DMF). The usefulness of such solvents can be explained by the fact that the influence of protonation is weakened, the study of the mechanism of the electrode process is simplified, and it becomes possible to observe multistage electron transfer and the formation of complexes with the central atom in the lowest valence states, which are unstable under the usual conditions. Nor can one rule out the possibility of the selection on the basis of polarographic data of conditions for the electrochemical generation of these unstable species and the study of their chemical structure. Finally, in organic media it is possible to extend greatly the range of m.d.e. polarisation potentials.

In the present review an attempt is made to discuss the present state of electrochemical studies on metal chelates in non aqueous systems—to assess the fundamental achievements and prospects in this relatively new field.

II. ELECTROCHEMICAL REDUCTION OF METAL CHELATES WITH ORGANIC LIGANDS IN NON-AQUEOUS MEDIA

In order to elucidate the influence of the chemical structure of metal chelates on the mechanism of their electrochemical reduction, it is necessary to study a fairly wide range of coordination compounds with various types of chelate units, determined both by the nature of the central atom and by the properties of the donor atoms in the analytically useful functional groups and their steric disposition in the molecule of the organic reagent. The authors

realise that not all the series of coordination compounds have been considered in equal detail in this review, because a complete treatment of all chelating agents is impossible and is hardly desirable. Most attention has been devoted to the chelates of *d* elements with filled and unfilled *d* shells.

1. Electrochemical Reduction of Metal Dithiocarbamates at the Mercury Dropping Electrode

The polarographic reduction of dithiocarbamates (DTC) at the mercury electrode in DMF has been studied in a series of investigations[2-5]. Chelates having the general formula $(R_2NCS_2)_nM^{n+}$ [$(CH_2)_4ONCS_2$]$_n$ and [$(CH_2)_mNCS_2$]$_nM^{n+}$, where $M^{n+} = Zn^{2+}$, Cd^{2+}, Sn^{2+}, Tl^{+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, or Ni^{2+}, R = CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9, and m = 4, 5, or 6, were investigated. It was found that, in terms of their electrochemical behaviour, they can be divided into two groups. The first includes the dithiocarbamates of metals with filled *d* shells: Zn^{2+}, Cd^{2+}, Sn^{2+}, Hg^{2+}, Tl^{+}, Pb^{2+}, Bi^{3+}, and Cu^{2+}. They give rise to waves, corresponding to the reduction of the central ion to the metal, on polarograms obtained in DMF in the presence of $(C_2H_5)_4NClO_4$ as the supporting electrolyte; the values of their $E_{1/2}$ vary in the range from −0.6 to −1.5 V. The reduction is nearly reversible (except for the Cd^{2+} and Zn^{2+} chelates):

$$M^{n+}(R_2NCS_2)_n + n\,e + Hg \rightleftarrows M^0(Hg) + nR_2NCS_2^-.$$

The nature of the ligand is reflected in the polarographic properties of the chelates. The greater stability of complexes with ligands having a stronger electron-donating group is the cause of the displacement of $E_{1/2}$ towards cathodic potentials (in the range 0.05–0.07 V) as R is varied in a homologous series. The standard rate constants for charge transfer k_S (based on oscillopolarographic data) are in the range $(1.2-2.6)\times10^{-2}$ cm s^{-1}. The form of the polarisation curves depends on the concentration of the complex, which is due to the adsorption activity of the DTC. The adsorbability is influenced by the nature of the solvent and R, which determine the solubility of the DTC. The reduction of this group of DTC takes place mainly in the range of E values close to the electrocapillary zero, where the adsorbability is manifested to the greatest extent.

Polarograms referring to the second group of complexes of the type $M^{n+}(R_2NCS_2)_n$, where $M^{n+} = Cr^{3+}$, Mn^{3+}, Fe^{3+}, Co^{3+}, or Ni^{2+}, consist of n plateaux corresponding to the successive transfer of n electrons. The reduction of Mn^{3+} chelates proceeds in two stages with the transfer of one and then two electrons. The product of the final irreversible stage is the metal on the mercury surface. The stepwise reduction of the DTC is complicated by the intervening dissociation of the intermediate complex species (the central atom in a low valence state) involving the formation of the $R_2NCS_2^-$ anion. The nature of the substituent at the nitrogen atom in the DTC molecule has some influence on the ease of reduction of complexes in DMF: an increase in the length of the aliphatic chain in the homologous series leads to a cathodic shift of $E_{1/2}$ for irreversible waves. The same shift occurs with increase in the size of the ring in heterocyclic derivatives. The lack of a simple correlation with the half-wave potentials of the one-electron reversible stage in the reduction of the dithiocarbamates of typical transition metals and the Taft constants of the substituents at the nitrogen atom can hardly be accounted for by the steric hindrance in the reduction reaction.

$E_{1/2}$ for the reversible one-electron process, characterising the energy of the lowest unoccupied molecular orbital, is apparently insensitive or only slightly sensitive to steric effects. The deviations of $E_{1/2}$ from the linear relation with the free energy are more likely to be due to a complex dependence of the adsorption of chelates on the nature of the groups involved and the influence of adsorbability on $E_{1/2}$.

Variation of the nature of the substituents R and R′ in the ligand fragment of iron(III) dialkyldithiocarbamates over a wide range made it possible to discover more refined factors influencing the reactivity of chelates of this type in the electrochemical reduction[6]. A study was made of the dependence of $E_{1/2}$ for the first reversible one-electron reduction stage on the energy difference between the ground and excited states. It was found that high-spin complexes are reduced more readily than low-spin complexes almost by 0.25 V. It was suggested[6] that the steric interaction with the sulphur atoms in low-spin complexes having bulky R and R′ groups leads to a non-planar structure of the fragment [C_2N-CS_2] and the electron pair of the atoms can be delocalised only within the limits of the chelate unit; the ligand field is therefore strengthened. For small substituents R and R′, a planar mesomeric structure (mesoionic form) of the type $C_2N^+ = CS_2$, with a shorter C–S bond, becomes preferable, so that the ligand field is weakened. To illustrate the influence of the steric effect of substituents on $E_{1/2}$, a comparison was made of the dithiocarbamates of the iron(III) complexes of pyrroline and 2,5-dimethylpyrroline[6].

Although in certain cases the reduction of chelates is in fact complicated by adsorption effects, the ease of reduction of dithiocarbamates of both groups at the m.d.e. is largely determined by the nature of the central atom, which is consistent with the "metallic" nature of the metal–ligand bond. However, the ease of reduction is apparently influenced in certain cases by the contribution of the mesomeric form of the ligand.

The results of a study of the electrochemical reduction of nickel dithiocarbamates by chronopotentiometry were published recently[7]. A study was made of the complexes with aliphatic straight-chain, branched, and alicyclic groups in DMF in the presence of 0.1 M $NaClO_4$ as the supporting electrolyte and platinum and stationary mercury electrodes. In all cases the authors[7] observed a single reduction wave, and not two, because the range of the possible polarisations of the electrodes in the presence of sodium perchlorate was insufficiently broad, i.e. the authors studied only the first stage of the reduction of the nickel chelates. It was found that the complexes are reduced irreversibly (with rare exceptions) and that the product $i\tau^{1/2}$ [where i is the current density and τ the duration of the arrest on the chronopotentiometric $E = f(t)$ curve] is independent of the current density. Consequently preceding dissociation of the complexes was not observed under the experimental conditions. It follows from these data[7] that the greater the stability of the chelates, the lower the charge-transfer rate constant. Having noted that in the series of complexes investigated the orbital to which an electron is transferred is mainly "metallic", the authors[7] believe that in certain cases there is a possibility of a shift of the location of the transferred electron from the metal to the ligand, for example, on passing from the dibenzyl derivative to the dicyclohexyl derivative. Comparison of the results of Budnikov and coworkers[3-5] and Ahmed and Magee[7] shows that the replacement of mercury by platinum leads to a significant change in the nature of the one-electron stage in the reduction of nickel

dithiocarbamates. The absence of a clear dependence of the ease of reduction at the platinum microelectrode on the structure of the ligand (with a large scatter of the peak potentials E_p along the potential axis) and the low rate of charge transfer apparently indicate a significant influence of the adsorption and kinetic contributions on the electrode process under these conditions[7].

In connection with the problem of the elucidation of the biological role of metals in enzymes, the oxidation-reduction properties of certain molybdenum and vanadium complexes of a number of sulphur-containing ligands, which form the inner coordination sphere, including dithiocarbamates, were investigated by electrochemical methods[8,9]. These complexes were regarded as models of metalloenzymes. The formation of dinuclear dimers, which determine the mechanism of the behaviour at the electrode, is characteristic of molybdenum(V) dithiocarbamate chelate complexes. Dinuclear complexes with DTC were not observed for vanadium in different oxidation states[9]. The transfer of the first electron to $V(R_2NCS_2)_3$ at the platinum electrode is reversible. The reduction of $VO(R_2NCS_2)$ proceeds in a complex manner and involves the formation at one of the stages of a certain amount of the $V(R_2NCS_2)_3$ species apart from the main product V_2O_3. The reduction of $VO(R_2NCS_2)_3$ results in the formation of $VO(R_2NCS_2)_2$ and the ligand anion. In the molybdenum complexes the DTC ligands give rise to a more "electron saturated" environment around the central ion than other ligands, for example 8-hydroxyquinoline[8].

2. Mixed-Ligand Metal Complexes with Dithiocarbamates in Electrochemical Reactions

When complexes are formed with variable-valence transition metal ions, those with metals in a high oxidation state (Cr^{3+}, Mn^{3+}, Fe^{3+}, and Co^{3+}) are as a rule stabilised. The introduction into the chelate molecule of ligands exhibiting π-acceptor properties [2,2′-bipyridyl(Bipy) and 1,10-phenanthroline(Phen)] promotes the stabilisation of the low oxidation state of the central atom. An example is provided by manganese(II) and iron(II) complexes $M(R_2NCS_2)_2Bipy$ or $M(R_2NCS_2)_2Phen$.[10] When they are reduced in DMF at the m.d.e., the polarograms show four plateaux corresponding to one-electron transfers in accordance with the mechanism $M^{2+} \rightleftharpoons M^{+}$ and $M^{+} \rightleftharpoons M$ and the reduction of Bipy or Phen. Similar heteroligand complexes are also formed by Zn^{2+}. In contrast to simple zinc(II) dithiocarbamates, they are reduced in stages with formation of an intermediate species in which the central atom has a formally low valence state. The unpaired electron in the product of the reversible electron transfer to $Zn(R_2NCS_2)_2Bipy$ is delocalised over the Bipy ligand and occupies an antibonding π^* orbital. In the electrolysis of a solution of this complex at the potential of the limiting current of the first one-electron wave, the $Bipy^{\cdot-}$ radical-anion was detected by EPR.[11,12]

Nickel(II) dithiocarbamates do not form heteroligand complexes with Bipy. However, in the presence of Bipy or Phen an increase in the limiting current of the first reversible one-electron wave at the expense of the second and an anodic shift of both branches are observed. Similar phenomena are also observed for the chromium(III) and cobalt(III) dithiocarbamates when the above π-acceptors are added to the polarographed solution. The increased current is due to the kinetic contribution. The results indicate a chemical reaction of π-acceptors with the one-electron transfer product (ECE mechanism):

$$M^{(n+1)}(R_2NCS_2)_n + e \rightleftarrows [M^{n+}(R_2NCS_2)_n]^-$$

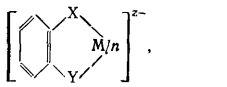
$$[M^{n+}(R_2NCS_2)_n]^- + Bipy(Phen) \xrightarrow{k} [M^{(n-1)}(R_2NCS_2)_{n-1}]Bipy(Phen) + R_2NCS_2^- .$$

The intermediates formed at the electrode in acetonitrile are more stable. The electrolysis of a solution of the chromium(III) complex at the potential of the limiting current of the first wave in the presence of Bipy exhibits a distinct spectrum of paramagnetic species containing lines due to splitting by the four nitrogen atoms. According to polarographic data, the heteroligand complex $Cr^{+}[(C_2H_5)_2NCS_2]Bipy$ is formed under these conditions. Since Cr^{3+}, having the d^5 electronic configuration, can form octahedral complexes, it follows that under the electrolysis conditions there is a possibility of the addition of yet another molecule and the formation of the complex species $Cr^{+}(C_2H_5)_2NCS_2(Bipy)_2$, whose signal is observed in EPR spectra[13].

Among other heteroligand complexes containing DTC, studies were made on compounds having the composition $[(Cp)_2VR_2NCS_2]^{+}$, where R = CH_3, C_2H_5, n-C_4H_9, or iso-C_3H_7, and Cp = cyclopentadienyl[14]. They are reduced in acetone in the presence of $(C_2H_5)_4NClO_4$ as the supporting electrolyte in two one-electron stages. The first reduction wave is fully reversible, while the second is irreversible. It is suggested that the reversible wave corresponds to the transfer of one electron to a non-bonding orbital of the vanadium atom with formation of a neutral vanadium(III) complex, tending to split off a free $R_2NCS_2^-$ anion. It was established by a.c. polarography that the dissociation is facilitated in the presence of oxygen. The free anion can oxidise metallic mercury to Hg^{+} at a potential more negative that $E_{1/2}$ for the first cathodic wave. The mechanism of the electrode process corresponding to the first wave has been described by an EC_1EC_2 scheme and is regarded as a special case of the ECE mechanism.

3. Dithiolates and Related Chelates

Dithiolate complexes, i.e. compounds with the chelate unit  , where M is a transition metal, have been the subject of numerous polarographic studies. The first investigations in this field are examined in two reviews[15,16]. The polarograms of complexes in this group have several waves, the first of which is as a rule reversible. The stepwise nature of the reduction process has been observed in a series of inner complexes in which the structure of the coordination shell is[17]



where M = Cu, Ni, Co, Pd, or Pt for $n = 2$ and V, Cr, Mo, or W for $n = 3$, with formation of species where $z = 1$ or 2 ($n = 2$) and $z = 1$, 2, or 3 ($n = 3$).

In methylene chloride the intermediate species are fairly stable. The influence of the donor atoms X and Y on the ease of transfer of the first electron was examined qualitatively in relation to nickel bis-complexes[18]. It was established that $E_{1/2}$ for the nickel chelates undergoes a "cathodic" shift in the following series of coordination cells:

$$[NiN_4] < [NiN_2S_2] < [NiS_4] \leqslant [NiO_2S_2].$$

In a subsequent study [19], these results were refined and in addition to the influence of the donor atoms in the chelate unit on $E_{1/2}$ was discussed in relation to the zinc, copper, palladium, and cobalt inner complexes with *o*-mercaptophenol, 1-mercapto-2-naphthol, and 1-hydroxy-2-pyridinethione.

Together with polarography, the EPR method was used in the studies under consideration [15-19]. The fact that the transfer of the first electron to the dithiolate is reversible with formation of a stable paramagnetic product in a suitable solvent permits the use of this electrode reaction for the electrochemical generation of such a product. Interest in the electrochemical generation of species of this kind is due primarily to the ease with which it can be followed. Application of the EPR method not only established the formation of paramagnetic species, but also yielded valuable information about the nature of these species, about the nature of the metal–ligand bond, etc.

Two studies have been published, in which cyclic voltammetry was used to investigate the mechanism of the one-electron transfer reactions involving cobalt [20] and nickel [21] maleonitriledithiolate (mnt) complexes. The method made it possible to study in detail the $[Co(mnt)_2]^{z-}$ ($z = 0$, 1, or 2) system in the absence and presence of pyridine (Py), to calculate the rate constant for the formation of heteroligand cobalt complexes with mnt and Py having the composition $[Co(mnt)_2Py]^-$ and $[Co(mnt)_2Py_2]^-$, and to propose a mechanism for the electrode process [20]. The triply charged anionic nickel complex with this ligand can be obtained by the reduction of the corresponding dianion at the electrode in acetonitrile or dimethoxyethane [21]. In the presence of traces of atmospheric oxygen this process takes place almost instantaneously. Analysis of the EPR spectra showed that the unpaired electron in the $[Ni(mnt)_2]^{3-}$ species is largely localised at the metal.

Polarography together with other methods has been used in the study of the dithiolene complexes of zirconium(IV), titanium(IV), and molybdenum in different valence states with toluene-3,4-dithiol in acetonitrile and methylene chloride [22]. Electrode transfer to the depolariser is irreversible in these processes.

4. Metal Diketonates in Electrochemical Reduction Reactions

The electrochemical behaviour of transition metal chelates with acetylacetone and certain dithiodiketones containing stable five-membered rings in their structure has been discussed in a review [23]. This section deals with studies carried out in recent years which are not included in the above review [23]. Thus interesting results were obtained in the investigation of the influence of substituents in the chelate ring in the series of trisdiketonate ruthenium(II) and ruthenium(III) complexes on the ease of reduction in DMF at a rotating platinum microelectrode [24]. Ruthenium complexes of this type, in both oxidation states, proved to be kinetically stable under the experimental conditions. The stage involving electron transfer to the ruthenium(III) chelate is reversible and uncomplicated by accompanying chemical reactions:

$$Ru(R_1COCHCOR_3)_3 + e \rightleftarrows Ru(R_1COCHCOR_3)_3^-.$$

$E_{1/2}$ varies over an unusually wide range (approximately 1.84 in DMF) as R_1 and R_2 are altered. The analogous range of variation of E was found to be at most 1.5 V in an earlier study [15] for a series of substituted chelates with a delocalised electronic structure of the type $M(S_2C_2R_2)_n$, where M is a transition metal (but not ruthenium). Electrochemical data for ruthenium(III) chelates of the type under consideration made it possible to employ the principle of the linearity of free energy in order to describe their reactivities in the one-electron transfer reaction. It has been stated [24] that cobalt(III) dithiocarbamate, for example, $Co[(C_2H_5)_2NCS_2]_3$, is reduced irreversibly in DMF at a platinum electrode with transfer of one electron. This finding is consistent with data for the reduction of nickel(II) dithiocarbamate under analogous conditions, discussed above [7].

The reduction of chromium(III) tris-β-diketonates was studied in dimethyl sulphoxide and 85% aqueous dioxan [25]. In the pure solvent the chelates CrL_3 (here HL = $R_1COCHR_2COR_3$; $R_2 = H$, $R_1 = R_3 = H$, CH_3, CF_3, or C_6H_5; $R_1 = H$, $R_3 = CH_3$, t-C_4H_9, or C_6H_5; $R_1 = CH_3$, $R_3 = CF_3$ or C_6H_5; $R_1 = CF_3$, $R_3 = C_6H_5$ or t-C_4H_9; $R_1 = R_3 = CH_3$, $R_2 = CH_3$, C_2H_5, or C_4H_9; $R_1 = C_6H_5$, $R_3 = CH_3$, $R_2 = CH_3$, C_2H_5, or C_4H_9; $R_1 = R_3 = C_6H_5$, $R_2 = CH_3$, C_2H_5, or C_4H_9) gave rise to one-electron waves, the first of which is associated with the reversible reduction

$$CrL_3 + e \rightleftarrows CrL_3^-.$$

On the other hand, in a mixed solvent the process is less reversible and the polarograms show one wave. The values of $E_{1/2}$ are in the range from −0.4 to −1.8 V, depending on the nature of R_1, R_2, and R_3. The effects of substituents are additive and are determined by their polarity. There is no correlation between $E_{1/2}$ and the usual parameters characterising the ligand field, while the spherical potential of the ligand field varies in parallel with the ease of reduction of the chelate. It is suggested [25] that the dependence of $E_{1/2}$ on the nature of R_1, R_2, and R_3 is associated with changes in electron density at the oxygen atoms of the pseudoaromatic chelate ring.

Vanadyl acetylacetonate in acetonitrile is reduced at the mercury electrode via a complex mechanism involving two electrons. In the presence of a diketone the process is complicated by intervening chemical reactions of the intermediates in the reduction process with acetylacetone [26]. Nickel(II) bis-β-dithiodiketonate complexes are reduced with electron transfer in stages involving the formation of intermediate charged complex species [27].

A comparative study of the influence of the nature of the oxygen and sulphur donor atoms on the ease of reduction in the general case led to the same conclusions as for the similar nickel complexes with a five-membered chelate unit [18,19], i.e. the replacement of O by S facilitates the reduction. The greater the number of sulphur atoms in the coordination unit of nickel β-diketonate, the less negative are the potentials at which the reduction takes place and the higher the charge transfer rate constants. In terms of the ease of reduction, these chelates can be arranged in the sequence $NiS_4 > NiS_2O_2 > NiO_4$. The same series is in essence retained for the values of k_S: $NiS_4 \simeq NiS_2O_2 > NiO_4$. [27] As for ruthenium β-diketonates [24], the values of $E_{1/2}$ for the first stage in the reduction of nickel(II) bis-β-dithiodiketonates in acetone cover a fairly wide range [28]. However, the dependence of $E_{1/2}$ on $\Sigma\sigma^*$ is not linear, despite the fact that the reduction at this stage leads to the formation of a thermodynamically stable oxidation-reduction pair.

Palladium(II) acetylacetonate is reduced irreversibly in DMF with consumption of two electrons (to form the metal amalgam) [29], which agrees with data for alcohol–benzene solutions [30].

5. Complexes with Schiff Bases

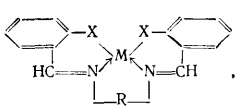
One of the first studies on chelates of this type concerned cobalt complexes with ligands which are structural analogues of one of the fragments of vitamin B_{12}.[31,32] An electrochemical model of the reduction processes involving the cleavage of the cobalt–carbon bond was studied in relation to the reduction of cobalt complexes of the type RCo^{2+}, where R = C_6H_5 or CH_3, with N,N′-ethylenebis(salicylideneamine) (H_2A) and 1,3-bisdiacetylmonoximeiminopropane (HB) in DMF. The C_6H_5–CoA chelate gives rise to three one-electron waves on the polarograms. The first two are of a diffusional and reversible type. According to data derived from cyclic voltamperograms and electrolysis at a controlled potential, the product of the one-electron transfer $[C_6H_5–CoA]^-$ is fairly stable. The dianion $[C_6H_5–CoA]^{2-}$, formed in the second reduction stage, is unstable under these conditions. The chelate CH_3–CoA is reduced in the first stage to $[CH_3–CoA]^-$, decomposing at the electrode with formation of a number of products: Co, CoA^-, and CH_3^-.

The second and third stages are poorly reflected in the curves. The chelate $[C_6H_5–CoB]^+$ gives rise to two reversible one-electron plateaux on the polarograms; the product of the two-electron transfer is fairly stable and can be isolated after electrolysis at a controlled potential. The electrochemical reduction of the $[CH_3–CoB]^+$ species proceeds via the mechanism

$$[CH_3–CoB]^+ + e \rightleftarrows CH_3–CoB,$$
$$CH_3–CoB + e \rightleftarrows [CH_3–CoB]^-.$$

The neutral species disproportionates with formation of $(CH_3)_2CoB$ and CoB. The same products are formed as a result of the interaction of the initial species and the monoanion. The different types of electrochemical behaviour of the chelates $[C_6H_5–Co]^{2+}$ and $[CH_3–Co]^{2+}$ with the above ligands are due to weaker electron-donating properties of phenyl compared with methyl. The electrode reactions of these coordination compounds simulate to some extent the biochemical action of vitamin B_{12}.[32]

The redox properties of complexes having the structure[33]



where M = Co, Ni, or Cu, X = O or NH, and R = $CH_2–CH_2$, $(CH_2)_3$, or $CH(CH_3)CH_2$, were investigated at a platinum electrode in methylene chloride. The low-valence state of the central atom in the bis-complexes of the same metals with the Schiff bases obtained from acetylacetone and salicylaldehyde and amines is stabilised at the m.d.e. on reduction via the process $M^{2+} \rightleftarrows M^+$; the stabilisation can be explained by the square-planar structure of the initial ligands[34].

The electrochemical reduction of cobalt chelates having the general formula RCoLX,[35] where R = C_6H_5, CH_3, C_2H_5, or $CH{=}CH_2$, L = the monoanion of 1-diacetyl monoximatoimino-3-diacetylmonoximeiminopropane or a tetradentate dianion [*N*,*N*′-ethylenebis(salicylideneaminate), *N*,*N*′-ethylenebis-(7,7-dimethylsalicylideneaminate), or *N*,*N*′-ethylenebis(acetylacetoneiminate)] and X is the solvent, was investigated by polarography at the m.d.e. in DMF, pyridine, and dimethyl sulphoxide. The nature of the group R and the solvent X influences the stability of the one-electron transfer product. The complex of the first ligand gives rise to two one-electron plateaux on the polarogram, the second of which corresponds to the formation of a species in which the degree of oxidation of the central atom is +1. The complex $[C_6H_5–Co]^-$, obtained as a result of electrolysis at a controlled potential E, was identified spectrophotometrically. The species $[RCoL]^-$, derived from chelates with R = CH_3 or C_2H_5, reacts in the course of electrolysis with the initial depolariser, forming bis-complexes. The values of $E_{1/2}$ for the first plateaux are satisfactorily correlated with the pKa of acids of the type RH.

In another study[36] the same workers described the polarographic behaviour of cobalt complexes having the composition $[Co^{3+}YL_2]^+$ and $[Co^{2+}Y_2]^0$, where Y is an equatorial ligand—the dianion of an imine of the same type as in earlier investigations[35] and L is an axial ligand: methylamine, n-propylamine, benzylamine, aniline, pyridine, and similar amines. The complexes are reduced in 95% ethanol via two reversible one-electron stages corresponding to a formal change in the degree of oxidation of cobalt:

$$[Co^{3+}YL_2]^+ + e \rightleftarrows Co^{2+}YL_2 \text{ and}$$
$$Co^{2+}YL_2 + e \rightleftarrows [Co^{+}YL_2]^- ,$$

but only in the presence of an excess of the amine L. In the absence of the amine, the first reduction stage is irreversible, which was explained by the subsequent chemical stage in which L is split off. At a platinum microelectrode under the same conditions[36] oxidation takes place with the reversible transfer of one electron via the formal mechanism:

$$Co^{2+} - e \rightleftarrows Co^{3+}.$$

The values of $E_{1/2}$ for the first reduction stage of these chelates with various Y reflect the influence of the electronic structure of the tetradentate ligand. An increase in the degree of conjugation in the structure of Y causes an "anodic" shift of $E_{1/2}$. The observed correlation between $E_{1/2}$ for the first stage and the pKa of the amines indicates a transfer of electron density from L to Y. This correlation occurs only for ligands with the same electronic and steric configurations of the nitrogen donor atom. The small change of $E_{1/2}$ for the second stage as a function of the nature of L shows that the interaction of the amine with cobalt is only slight. The authors[36] suggest that $E_{1/2}$ for the first stage characterises the energy of the unoccupied molecular orbital.

The electrochemical reduction of 37 mononuclear and dinuclear copper(II) complexes with imino-ligands L (L = substituted β-ketoamines, β-iminoamines, or pyrrole-2-aldimines) in DMF in the presence of tetra-n-propylammonium perchlorate as the supporting electrolyte was investigated by electrochemical methods and ultraviolet spectroscopy[37]. The mononuclear complexes are reduced with consumption of one electron. The dinuclear chelates are reduced with transfer of two electrons in one of two consecutive stages as a function of the nature of L with formation of the corresponding copper(I) chelates. Complexes of this type, which have a non-planar structure, are reduced more readily than planar chelates. The ease of their reduction increases in the sequence rigid tetradentate (with N_4 units) < bidentate (with N_2O_2 units) < bidentate (with N_2S_2 units) ligands.

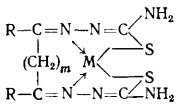
6. The Behaviour of Thio- and Seleno-semicarbazone Metal Complexes at the Mercury Dropping Electrode in DMF

The ligand in complexes of thio- and seleno-semicarbazones is in many cases the protonated form of the initial organic reagent. For this reason they exhibit different types of behaviour at the electrode[38-42]. Metal complexes with the thiosemicarbazones of acetone (Hthac), benzaldehyde (Hthbz), anthranilic aldehyde (Hthan), salicylaldehyde (Hthsa), and their selenium analogues give rise to different numbers of waves on polarograms in DMF in the presence of $(C_2H_5)_4NClO_4$ as the supporting electrolyte. The polarograms of copper(I) chelates with Hthac and Hthbz contain two waves. Their first one-electron waves are nearly reversible:

$$\underset{(L = \text{ligand})}{CuL} + e + Hg \rightleftarrows Cu(Hg) + L^- \ .$$

The second waves, at negative potentials, are due to the ligand liberated in the first stage. They are of the kinetic type and differ from the waves of the initial Hthac and Hthbz by their parameters owing to the deprotonation of the reactants on complex formation. The copper(II) chelate complex of H_2thsa gives rise to one two-electron wave on polarograms. The thio- and seleno-semicarbazones of anthranilic aldehyde react with Cu^{2+} to form complexes $Cu(HL)Cl_2$, i.e. without the displacement of hydrogen ions. They give rise to an extended irreversible wave on polarograms, corresponding to the reduction of the central ion, and a wave due to the reduction of the ligand with $E_{1/2}$ close to that of the initial Hthan or Hsesan.

The mechanism of the reduction of copper(II) complexes of bisthiosemicarbazones under the conditions corresponding to the first wave is probably analogous to the mechanism of the reduction of copper(I) chelate complexes of Hthac and Hthbz. The constant k_S for this stage is $(0.50 \pm 0.16) \times 10^{-2}$ cm s^{-1}. $E_{1/2}$ diminishes with increase of the number of methylene groups in the ligand fragment of the chelate. The structures of copper(II) complexes of bisthiosemicarbazones have in general three chelate rings[39]:



For $m = 0$ or 1, the middle ring is five- or six-membered, i.e. is the most stable, and this factor is responsible for the maximum chelating effect. With increase of m to three, the middle ring expands and makes no contribution to the stabilisation of the chelate structure. The possibility of forming complexes of this type promotes the stabilisation of the central atom in the +2 oxidation state. For $m = 4$, this does not happen: the bisthiosemicarbazone behaves similarly to Hthac or Hthbz, i.e. copper(II) is reduced to copper(I) with formation of the corresponding complex. The thiosemicarbazones of salicylaldehyde and anthranilic aldehyde (H_2thsa and Hthan) and their selenium analogues form the cobalt complexes $[Co(HL)_2]X$, in which the metal is in the +3 oxidation state. Their polarograms contain two waves. The first extended, irreversible wave (with $E_{1/2} \simeq -1.1$ V) formally corresponds to the reduction of the metal ion in the complex and the second at $E \simeq -1.5$–-2.0 V corresponds to the electrochemical reaction of the ligand anion.

The cathodic shift of $E_{1/2}$ on passing from cationic complexes of the type $[Co(Hthsa)_2]Cl$ to the anionic complexes $NH_4[Co(thsa)_2]$ can apparently be accounted for not only by the formation of a more stable complex in the latter case, but also by the sign of the charge of the species being reduced. The results of the investigation showed that $E_{1/2}$ is independent of or depends little on the nature of outer-sphere ion X.[41] Nickel ions react with reagents of this type to form complexes of two kinds: with and without substitution of the hydrogen atoms in the ligand. The complexes $[Ni(HL)_2]Cl_2$ give rise to two irreversible waves on the polarograms. The first diffusional stage formally corresponds to the process $Ni^{2+} \rightarrow Ni^0$, while the second is due to the ligand.

For nickel chelate complexes of bisthiosemicarbazones, the stepwise transfer of two electrons is observed. The stepwise mechanism of the reduction indicates the formation of intermediate complex species with a formally low-valence state of the central atom[42]:

$$NiL + e \rightleftarrows [NiL]^- + e \rightleftarrows [NiL]^{2-} \ .$$

The electrochemical behaviour of cadmium, lead, and nickel complexes with reagents of the above type has been described[40].

Comparison of the polarographic behaviour of metal chelate complexes (having structures of the same type) of various thiosemicarbazones reveals the following regularity. If the metal does not form an amalgam with mercury or its solubility in mercury is low, then the product of the two-electron transfer exists for a time at the electrode, which is the reason for the reversibility of the process (nickel chelates having the structure of the inner complex type). Subsequent electron transfer to the chelate dianion formed should apparently occur at very much higher negative potentials E, so that there are no waves due to the ligands. On the other hand, if the metal is readily soluble in mercury (for example, lead and cadmium), then the formation of an amalgam promotes the deactivation of the two-electron transfer product with formation of species differing from the initial thiosemicarbazone and being reduced at more "cathodic" potentials E. The difference between them can be explained by the fact that the ligand in the inner complex structure is a deprotonated thiol form of the thiosemicarbazone. In those cases where complex formation proceeds without the elimination of protons, the ligand and the initial thiosemicarbazone give rise to virtually identical waves on the polarograms.

7. Metal Chelate Complexes of Certain Hydroxyazo-Compounds in DMF

In terms of their electrochemical behaviour, these complexes like the metal complexes of dithiocarbamates and thiosemicarbazones can be divided into two groups, depending on the electronic configuration of the central atom[43-45]. Cadmium(II), lead(II), tin(II), and copper(II) complexes are reduced in DMF at the m.d.e. in two stages. The first stage corresponds to the transfer of two electrons and formally involves the electrochemical reduction of the central ion in the chelate. The second wave is due to the ligand L, liberated when the complex is reduced in the first stage. The parameters of the two waves differ from those of the initial azo-compounds.

The nature of the ligand is reflected in the polarographic properties of the chelates. The greater stability of complexes with ligands forming an additional coordinate bond due to the lone electron pair of the nitrogen atom in the heterocycle is the cause of the shift of $E_{1/2}$ towards more "cathodic" values. The introduction of a sulphur atom into the heterocycle reduces the electron-donating

properties of nitrogen in this ring and diminishes the strength of the M–L bond, which is reflected in the value of $E_{1/2}$.

The irreversibility of the second stage in the reduction of chelates in this group and its kinetic nature are evidently due to the decomposition of negatively charged complex species formed in the first stage, as in the reduction of chelate complexes of thio- and seleno-semicarbazones:

$$ML_n + 2e \rightleftarrows [ML_n]^{2-} + Hg \xrightarrow{k'} M^0(Hg) + nL^{(3-n)-};$$
$$n = 1, 2.$$

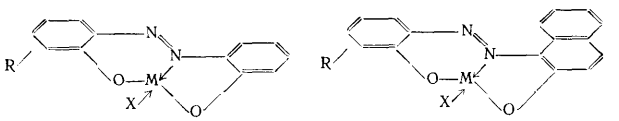
Manganese(II), nickel(II), and zinc(II) complexes, which constitute a second group of compounds, are reduced, in contrast to the previous compounds, via two irreversible one-electron stages, which are followed by a third irreversible wave. Comparison of the EPR spectra of the products of the one-electron reduction of nickel(II) and zinc(II) complexes with the EPR spectra of the products of the reduction of the initial azo-compound shows that the spin density of the transferred electron is localised at the ligand[46]. Taking into account the fact that the values of $E_{1/2}$ for chelates of this type with different metals differ insignificantly, presumably in this case the M–L bond is of the ligand type. Compared with the complexes of *o*-hydroxyazo-compounds, the chelate complexes of *o*,*o*′-dihydroxyazo-compounds are reduced at more negative potentials, since they form a more stable structure with metal ions, in which two pseudoaromatic rings are generated.

The limiting current of the first reduction wave of the nickel(II) and zinc(II) complexes of *o*,*o*′-dihydroxyazo-compounds exceeds the current of the second wave and the one-electron level. This is caused by the disproportionation of the products formed in the first stage. The disproportionation constants are in the range $(1-20) \times 10^4$ litre mole^{-1}s^{-1}. For certain rates of polarisation of the electrode, it is possible to eliminate almost completely the influence of the subsequent reactions and the electrode process can be regarded as reversible. For this range of rates, the equation of the linear relation between the free energy and the Hammett substituent constants can be put in the form

$$\Delta E_p' = \rho_\pi \sigma_R,$$

where $\Delta E_p'$ is the shift of the E peak on the oscillopolarograms under the influence of the substituents. This makes it possible to estimate the influence of substituents on the ease of the electrochemical reduction of the complexes, whose reduction under the conditions of classical polarography is complicated by the subsequent chemical reactions of the primary products of the reversible charge transfer[47].

The introduction of *m*- and *p*-substituents into the benzene ring of the ligand in chelates of the type



(where M = Ni, Zn, or Mn in the +2 oxidation state, X is the solvent, and R = *p*-NH_2, *p*-OH, *m*-Cl, *m*-Br, or *m*-I) alters E_p, but hardly influences other process parameters. The sensitivity of the reaction centre to the influence of substituents for zinc(II) complexes is somewhat smaller than for the analogous nickel(II) and manganese(II) chelates. The increase of $\rho_\pi(\rho_\pi^*)$ for chelates of the latter type can be accounted for by the increase of the electron density at the reaction centre owing to the involvement of the *d* electrons of the metals in the conjugation system. Owing to the characteristics of its electronic structure, the possibility of $p_\pi - d_\pi$ binding involving Zn^{2+} is smaller than for transition *d* elements, which is reflected in the sensitivity of the reaction centre to the influence of substituents[47].

8. Metal Complexes of 2,2′-Bipyridyl and 2,2′,2″-Terpyridyl in Electrochemical Reactions

Extensive studies on the polarographic behaviour of the chelates of typical transition metals have been carried out by Japanese investigators. Their earlier publications and those of other workers are discussed in a review[23]. Among the later studies on the polarography of bis-complexes, mention should be made of those concerning cobalt(II) and manganese(II) chelate complexes of bis-2,6-(2′-quinolinyl)pyridine[48], dicyanobispyridyl complexes of cobalt(III),[49] dichlorobispyridyl complexes of chromium(III),[50] and tungsten(V) and tungsten(IV) hexachloride complexes with Bipy in acetonitrile[51]. When the heteroligand complex $[Co(CN)_2(Bipy)_2]^+$ is reduced at the m.d.e. in dimethyl sulphoxide[48], three diffusion waves are observed. Each corresponds to the transfer of one electron, as for the cobalt(III) cyanide and bipyridyl complexes:

$$[Co(CN)_2(Bipy)_2]^+ + e \rightarrow Co(CN)_2(Bipy)_2 + e \rightarrow [Co(CN)_2(Bipy)_2]^- + e \rightarrow [CO(CN)_2(Bipy)_2]^{2-}.$$

In the concluding stage of the process, metallic cobalt is partly deposited, since the last complex is unstable under the experimental conditions. The formation of species with the central atom in the zero oxidation state has been confirmed oscillopolarographically.

In the presence of water, the one-electron reduction is accompanied by rapid disproportionation of the ligand and substitution by water molecules, which leads to the formation of an equimolar mixture of $[Co(CN)_4(Bipy)_2]^{2-}$ and $[Co(Bipy)_2(H_2O)_2]^{2+}$. The polarographic characteristics of the bipyridyl complexes in DMF can be found for ruthenium(III) in the paper of Patterson and Holm[37] and for osmium(IV) and iron in the paper of Misono et al.[52] Chelates with ligands of this type have been studied by electrically generated luminescence[53]. Its intensity depends on the stability of the intermediate species, which is determined in its turn by the nature of the ligand.

In the electrochemical studies examined above the metal in the initial depolariser was in the usual oxidation state, equal to two or three. Species with the central atom in a lower oxidation state arose at the electrode during electrochemical reduction; in certain cases they could be identified on the basis of their spectra.

For example, the absorption spectra of electrochemically generated unstable species were obtained in the reduction of bipyridyl complexes of cobalt(II) at a silver electrode in propylene carbonate[54].

There has been recently a renewed increase of interest in the study of electrode reactions of complexes of metals in a low oxidation state and in the determination of factors stabilising these complexes. The reversible one-electron reduction of heteroligand nitrosylbipyridylruthenium complexes having the overall formula $[Ru(Bipy)_2(NO)X]^{3+}$, where $X = Cl^-$, N_3^-, NO_2^-, NH_3, Py, or acetonitrile, was investigated by cyclic oscillopolarographic methods using a platinum electrode in acetonitrile[55]. It has been shown by EPR and infrared spectroscopy that the transfer of electrons is localised at the nitrosyl group.

Using the same methods as in the above study[55] and in addition the coulometric procedure, it has been shown[56] that the two consecutive one-electron stages in the reduction of diphenylbisbipyridylchromium(III) in acetonitrile and dimethyl sulphoxide occur at $E_{1/2} = 1.21$ and 1.64 V (relative to the saturated calomel electrode), regardless of the nature of the solvent and the material of the electrode, via the mechanism

$$[(C_6H_5)_2\,Cr\,(Bipy)_2]^+ + e \rightleftarrows [(C_6H_5)_2\,Cr\,(Bipy)_2]^0 + e \rightleftarrows [(C_6H_5)_2\,Cr\,(Bipy)_2]^-.$$

The higher degree of solvation of the depolariser in dimethyl sulphoxide compared with that observed in acetonitrile is reflected in the diffusion coefficient: 2.0×10^{-6} and 1.5×10^{-5} $cm^2 s^{-1}$ respectively.

A series of studies[57-62] devoted to the polarographic properties of transition metal complexes with different (ranging from +2 to −1) oxidation states of the central atom in the initial depolariser and also to the investigation of the kinetics of electron transfer in the corresponding oxidation-reduction pairs of the type $[M(Bipy)_3]^{n+}/[M(Bipy)_3]^{(n-1)+}$ arising at the electrode, have been published recently. The potentials $E_{1/2}$ of the first reversible one-electron stages in the reduction of Bipy, 4-methyl-2,2′-bipyridyl, 5-methyl-2,2′-bipyridyl and the corresponding iron(II), ruthenium(II), and osmium(II) complexes[67] in DMF have been compared. If it is assumed that the reduction of a chelate involves only the coordinated ligand, then there should be a linear relation between the electron affinity of the complex and that of the free ligand in the series of chelates of the same metal. Such a relation has been observed experimentally for iron, ruthenium, and osmium complexes with ligands of the same type:

$$E^{red}_{1/2,c} = E^{red}_{1/2,L} + C,$$

where the subscripts c and L refer to the $E_{1/2}$ of the complex and the free ligand and C is a constant. Since $E_{1/2}$ for complexes of metals M in the same oxidation state with any one ligand L varies by not more than 80 mV, for metals in the iron–ruthenium–osmium series, an electron is transferred to a molecular orbital of the π^*-ligand type.

The tris-complexes of chromium(I), chromium(0), vanadium(0), titanium(0), and molybdenum(0) have been studied by polarographic and cyclic voltamperometric methods[58] in DMF and tetrahydrofuran. Multiplateau waves are observed on the polarograms of these complexes in both the cathodic and anodic potential ranges, corresponding to multistage electron transfer. The half-wave potentials for reversible oxidation-reduction systems arising at the electrode have been determined. An empirical rule has been derived for the assessment of the nature of the orbital occupied by the electron transferred in the electrochemical reaction on the basis of $E_{1/2}$ for the complex with a methyl group introduced into the Bipy molecule. Thus, the transferred electron occupies an antibonding ligand orbital in the reduced forms of the redox pairs VL_3^-/VL_3^{2-}, CrL_3/CrL_3^-, CrL_3^-/CrL_3^{2-}, and CrL_3^{2-}/CrL_3^{3-}, where L = Bipy. In the corresponding VL_3^{2+}/VL_3^+ and VL_3^+/VL_3 complexes it occupies the t_{2g} orbital, which is of a metallic type. The difference between the energy levels of the orbitals of the complexes has been discussed quantitatively on the basis of the shift of their $E_{1/2}$ in relation to the $E_{1/2}$ of the free ligands. In the series of complexes $V(Bipy)_3^-$, $Cr(Bipy)_3$, and $Fe(Bipy)_3^{2+}$ the energy of the lowest unoccupied molecular π^* orbital is increased[58].

The values of k_S for trisbipyridyl chromium complexes have been determined by the method of the double galvanostatic pulse[59] at the m.d.e. and for analogous iron, ruthenium, osmium, chromium, titanium, vanadium, and molybdenum chelates[58] at a platinum electrode in DMF. In a series of these complexes k_S is independent (or depends little) of the oxidation-reduction potential of the corresponding redox pair, which varies from +1.03 to −1.54 V, of the degree of oxidation of the central atom in the oxidised form of the complex, of the nature of the solvent, and of the type of the electrode. This shows that the rate of charge transfer in the reduction of the complexes is largely determined by the electronic configuration of the reacting species. For species where the transferred electron is localised in the molecular orbital of the ligand π^* type, the values of k_S lie in the range 0.1 to 0.3 cm s^{-1}. For complexes in the reduction of which an electron is transferred to a molecular orbital of the metallic t_{2g} type, the values of k_S are in the range 0.8–1.3 cm s^{-1}. The constant k_S for the Bipy/$Bipy^-$ system is virtually the same as the value for the first group of the complexes investigated (~ 0.15 cm s^{-1}). On the basis of this finding, it has been suggested[58] that the contribution of the energy of reorganisation of the solvent† to the change in k_S is not as large as might have been expected. It is noteworthy that the values of k_S for the $[Fe(Bipy)_3]^{2+}/[Fe(Bipy)_2]^+$, $[Fe(Bipy)_3]^{3+}/[Fe(Bipy)_3]^{2+}$, and $[Cr(Bipy)_3]^+/[Cr(Bipy)_3]^0$ systems are close to the k_S for the Bipy/$Bipy^-$ redox system[58]. This difference can be accounted for by the fact that, in the oxidation of the $[Fe(Bipy)_3]^+$ species, an electron leaves a ligand π^* orbital, whereas in the reduction of the corresponding $[Fe(Bipy)_3]^{2+}$ species, an electron passes to a metallic t_{2g} orbital.

Information about the formation of bipyridyl complexes with a metal in a low oxidation state can be found for zerovalent vanadium[61], for Co^-,[63] for ruthenium in heteroligand nitrosoarene complexes with Bipy[64], and for manganese and chromium in complexes with certain aromatic tridentate ligands[65].

The overall mechanism of the reduction of metal bis-complexes with terpyridyl (Terpy) is similar to the mechanisms quoted above for reduction with stepwise electron transfer, for example, for chromium(III) chelates[65]:

$$[Cr(Terpy)_2]^{3+} + e \rightleftarrows [Cr(Terpy)_2]^{2+} + e \rightleftarrows [Cr(Terpy)_2]^{+}.$$

Manganese(II), cobalt(II), nickel(II), and europium(III) chelates of terpyridyl in acetonitrile have been investigated by different versions of the polarographic method[66]. Reversible electron transfer is observed for the first two stages in the reduction of manganese and cobalt complexes, but anions of the type $[Co(Terpy)_2]^-$ have not been detected. The reduction of the complex $[Eu(Terpy)_2]^{3+}$ involves the initial formation of $[Eu(Terpy)_2]^{2+}$. This species reacts further at the electrode with consumption of two electrons and the formation of zerovalent europium. The standard rate constant for this stage is 6.7×10^{-4} cm s^{-1}, which shows that it is clearly irreversible. The subsequent waves at the edge of the range of negative potentials are due to the reduction of the Terpy species. It has been concluded[66] that the d elements in the zero oxidation state exhibit a greater tendency towards complex formation than the f elements.

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† In reactions of the complexes one distinguishes processes involving the reorganisation of the inner and outer coordination spheres. The latter includes also the reorganisation of the solvent in which the complex is dissolved.

Like bipyridyl, another heterocyclic ligand—1,10-phenanthroline—is capable of stabilising the low oxidation states of transition metals[67]. The electrochemical reactions of these complexes resemble processes with participation of bipyridyl analogues[67,68]. It has been suggested[69] that the significant involvement of the π binding of the metal in the lowest oxidation state to the ligand as well as the ability of phenanthroline and its alkyl-substituted derivatives to delocalise the charge on the central atom even in the presence of a tetrahedral environment (in bis-complexes) are factors stabilising the intermediate electrode products. The polarograms of the tris-complex of iron(II) of 4,7-diphenyl-1,10-phenanthroline contain six reversible one-electron plateaux, each of which corresponds to a successive stage in the oxidation state of the metal from 2+ to 4−, i.e. the final species obtained in the reduction of the tris-chelate has six electrons in excess of the number characteristic of the usual oxidation state[67]. This quantity Δ (in the given case Δ_6) is the maximum attained electrochemically for low-spin metal complexes.

9. Metal Complexes of Phosphines in Electrochemical Reduction Reactions

The metal complexes with substituted phosphines as one of the ligands have become much investigated by electrochemical methods in recent times. Interest in these compounds is because they can be extremely active homogeneous catalysts of reactions of unsaturated organic compounds. Furthermore, such complexes, with the central atom in a low oxidation state, can be used to bind carbon monoxide as well as nitrogen in an active form.

Using mainly classical polarography and cyclic voltamperometry, a group of Italian investigators carried out a series of studies on the electrochemistry of coordination compounds of this type in non-aqueous media[70-75]. Under an argon atmosphere, in a 50% mixture of toluene and acetonitrile containing a certain amount of triphenylphosphine, a study was made of *trans*-chlorocarbonyl-bis(triphenylphosphine)rhodium(I) $RhCl(CO)[P(C_6H_5)_3]_2$. Its reduction takes place with addition of two electrons in one stage and the formation of a complex anion with the metal in the formal 1-oxidation state. The anion reacts further with the depolariser, which leads to a species in which rhodium is in the zero oxidation state[70]. Rhodium(I) and iridium(I) complexes of bisdiphenylphosphinoethane $(C_6H_5)_2P-CH_2-CH_2-P(C_6H_5)_2$, another π-acceptor, have the composition ML_2Cl and the polarograms also exhibit a single two-electron reversible diffusion wave in acetonitrile[71]. The addition of water leads to the disappearance of anodic peaks from the cyclic curve. During electrolysis at a controlled potential in solutions of the complexes, the colour of the solution changes and precipitates are formed. Apart from bands characteristic of the ligand in L, bands corresponding to rhodium and iridium hydrides were identified in the infrared spectra of the electrolysis products. The authors[71] suggest the following mechanism of the reduction at the m.d.e. in the presence of proton donors:

$$(ML)_2^+ \overset{2e}{\rightleftarrows} (ML)_2^- \xrightarrow{\text{proton donors}} MHL_2.$$

Data for the oxidation-reduction behaviour of these compounds have been compared with the reactivities of the anionic complexes in which the metal is in the 1-oxidation state and which have the d^{10} configuration[71].

In contrast to rhodium and iridium complexes[71], the cobalt complexes of bisdiphenylphosphinylethane having the general formula CoL_2ClO_4 are reduced with the reversible transfer of two electrons in stages[73]. The product of electrolysis at a controlled potential E, corresponding to the limiting current of the first wave and isolated in the form of red crystals, was identified as CoL_2 in which the central atom is in the zero oxidation state. At the potential of the second wave the unstable species $[CoL_2]^-$ is formed at the electrode and reacts with the solvent, which leads to the formation of $CoHL_2$. Thus the stabilisation of low valence states of the metals in electrochemical reduction reactions can be attributed to the high π^*-acceptor capacity of ligands of the given type.

A parallelism between the results of kinetic measurements and polarographic data has been observed[74] in the study of the following platinum(II) complexes: in 1,2-dimethoxyethane at the m.d.e (L = piperidine): *trans*-$\{Pt[P(C_2H_5)_3]_2Cl_2\}$, *trans*-$\{PtL[P(C_2H_5)_3]Cl_2\}$, and *trans*-$[PtL_2Cl_2]$. The ease of reduction diminishes in the series of these compounds, i.e. the phosphine complex is reduced more readily than, for example, a heteroligand complex with piperidine. The authors suggest that the rate of nucleophilic S_N^2 substitution of the phosphine-complex is sensitive to changes in the nature of the entering group.

An irreversible two-electron diffusion wave is observed in the reduction of a tetrakis(triphenyl phosphite) complex of rhodium(I) at the m.d.e. It is suggested that it is highly solvated in acetonitrile[75]. The product of the addition of two electrons $[RhL_4]^-$, where L is triphenyl phosphite, was identified after electrolysis at a controlled potential. Platinum complexes of triphenylphosphine in DMF at the m.d.e are reduced with the consumption of two electrons and the formation of the corresponding zerovalent platinum complex[76]. In the presence of water the product of the two-electron reduction is converted into a hydride complex having the composition $Pt[(C_6H_5)_3P]_2H(Cl)$. Comparison of the values of $E_{1/2}$ for the above compound and the initial depolariser shows that the introduction of a hydride ion into the inner coordination sphere of this complex causes a marked hindrance of the charge-transfer process.

III. ANODIC REACTIONS OF METAL COORDINATION COMPOUNDS

Much less attention has been devoted to anodic processes in the electrochemistry of metal complexes with organic ligands than to reduction processes. The main reason for this is that in the case of the m.d.e. a comparatively limited range of polarisation potentials is available. On the other hand, the use of solid electrodes for these purposes began quite recently. There has been a growth of interest in recent times in the investigation of the anodic process involving a wide variety of complexes in organic and mixed solvents, including electrochemical oxidation at solid electrodes, particularly for compounds in which the central atom is in a low oxidation state.

In the anodic oxidation of metal complexes an electron may be abstracted both from the orbitals of the central atom and from molecular orbitals of the ligand type. The products exhibit different stabilities. Useful information about the structure of these species can be obtained by EPR. The dependence of the oxidation potentials on the ionisation potentials is frequently linear. This finding confirms the validity of the idea that the primary stage in

the oxidation of the complex involves the abstraction of an electron from the highest occupied molecular orbital.

The oxidation-reduction properties of typical transition metal dithiocarbamates have been studied for the first time comparatively recently at a platinum electrode in acetone as a function of the nature of the complex-forming ion and substituents R and R′ in the ligand fragment of the chelate[77]. Judging from the results, the majority of the electron transfer reactions are rapid. The products of one-electron oxidation of many dithiocarbamates in acetone have comparatively short lifetimes (determined from cyclic voltamperometric data). The nature of the substituents R and R′ affects the ease of oxidation of the metal dithiocarbamates. However, a simple Taft correlation between $E_{1/2}^{ox}$ and the sum of the Taft substituent constants was not found. According to the authors[77], this is associated with the steric effects of the alkyl groups in the one-electron transfer reactions. In the series investigated the complexes of all the metals with *N*,*N*-dicyclohexyldithiocarbamate are oxidised most readily, while the chelates with *N*,*N*-dibenzyldithiocarbamate are oxidised with the greatest difficulty. Diethyldithiocarbamate derivatives occupy an intermediate position. The opposite relation has been observed for the reduction of the same compounds. In the series of the metal dithiocarbamates investigated the values of $E_{1/2} = E_{1/2}^{ox} - E_{1/2}^{red}$ depend significantly on the nature of the metal atom:

M	Cr	Mn	Fe	Co	Ni	Cu
$E_{1/2}$, V	2.58	0.48	0.92	2.02	2.34	1.07

This demonstrates the predominantly metallic nature of the molecular orbital in which the electron transferred in the electrochemical step is localised.

The oxidation of nickel(II) diethyldithiocarbamate has been investigated in no less detail at a platinum electrode than in acetonitrile[78]. Like the corresponding copper and iron chelates[79,80], the nickel(II) compounds are oxidised electrochemically comparatively readily and this can serve as a basis of the synthesis of metal dithiocarbamates with a high oxidation state of the central atom. The first stage in the oxidation of nickel(II) dithiocarbamates is reversible abstraction of one electron. Coulometric measurements at the limiting one-electron oxidation current yield $n = 1.3$. In the presence of $(C_2H_5)_4NBF_4$ electrolysis at a controlled potential leads to two products: $Ni^{4+}[(C_2H_5)_2NCS_2]_3BF_4$, in which the formal oxidation state of the metal is 4+, and $Ni^{2+}(BF_4)_2$ with an oxidation state of 2+. Nickel(IV) chelates have been isolated and identified.

In the anodic reactions of chromium, molybdenum, and tungsten complexes having the composition $L_2M(CO)_2$, where L = bis(diphenylphosphino)methane, the stepwise abstraction of two electrons is accompanied by the isomerisation of the *cis*-cation in the complex to the *trans*-cation; the *trans*-isomers of complexes with this ligand L are oxidised more readily than the similar complexes with bis(diphenylphosphino)ethane[81]. Using cyclic voltamperometry, electrolysis at a controlled potential, EPR, the oxidation of cobalt(III) and rhodium(III) chelate complexes with derivatives of dimethylglyoxime and salicylideneaniline has been investigated[82,83] at a platinum electrode in acetonitrile, methylene chloride, and a mixture of the latter with toluene. The supporting electrolyte was a 0.1 M $(C_2H_5)_4NBF_4$ solution.

Previously unknown complexes with formally quadrivalent cobalt and rhodium, in which the metal–carbon σ bond is retained, were observed in the reversible one-electron oxidation of chelates of the type $RCoL_2Py$ (R = CH_3, C_2H_5, or $C_6H_5CH_2$; L = bisdimethylglyoximate dianion), RCoL [R = CH_3, C_2H_5, iso-C_3H_7, or n-C_4H_9; L = bis(salicylidenato)ethylenediamine dianion], and RRhLPy [R = CH_3, n-C_3H_7, or iso-C_3H_7; L = bis(salicylidenato)ethylenediamine dianion]. The lifetime of these species has been estimated as amounting to several minutes. The stability of the complex species with the metal in the 4+ oxidation state and the ease of the oxidation of the initial chelates increase as R is varied in the sequence $CH_3 < C_2H_5 <$ n-C_3H_7 < n-C_4H_9 < iso-C_3H_7. On the basis of these data, it is suggested that during oxidation at the electrode an electron is abstracted from the central atom or from the group R and not from the chelating ligand. The product of the oxidation of the complexes is an analogue of the carbonium ion R^+.[82]

It is fairly interesting to compare the oxidation potentials of the complexes and the frequencies of the charge-transfer bands in the ultraviolet spectra. Such a correlation has been drawn for the trisbipyridyl complexes of iron, osmium, ruthenium, cobalt, and chromium, in which the metal is in the 2+ oxidation stage[83]. It is known that the minimum energy corresponding to the frequency of the charge-transfer band can be represented by the difference $\nu = I_c - A_L^c$, where I_c is the vertical ionisation potential of the t_{2g} orbital in the metal complex and A_L^c is the electron affinity of the lowest antibonding π^* orbital in the coordinated ligand. It is suggested that, during the oxidation of the complex, an electron leaves the t_{2g} orbital. Furthermore, it is believed that there is a linear relation between the electron affinities of the coordinated ligand and the organic compound not bound in the complex, in a series of chelates of the same metal with different ligands, which is expressed by the following relation:

$$E_{1/2,c}^{ox} - E_{1/2,L}^{red} = \nu + C,$$

where *C* is a constant. A simple correlation between $E_{1/2,c}$ and ν has not been observed for the complexes $[FeL_3]^{2+}$, $[RuL_3]^{2+}$, $[OsL_3]^{2+}$, $[CrL_3]^{2+}$, and $[CoL_3]^{+}$.[84] However, if one uses the difference $E_{1/2,c}^{ox} - E_{1/2,L}^{red}$ instead of $E_{1/2,c}^{ox}$, then the former is linearly correlated with the energy corresponding to the frequency of the charge-transfer band.

Thus there is a linear relation between this energy characteristic and the oxidation potentials of the complexes corrected for the electron affinity of the π-acceptor ligand. If an electron leaves the t_{2g} orbital during oxidation, then $E_{1/2}^{ox}$ for the tris-complex of a transition metal with bipyridyl undergoes a cathodic shift in the following sequence when a methyl group is introduced into the ligand: Bipy < 5,5′-CH_3-Bipy < 4,4′-CH_3-Bipy. The empirical rule concerning the influence of substitution on $E_{1/2}$ is used as a criterion in the determination of the configurations of transition metal complexes of bipyridyl on the basis of electrochemical data[84].

Data have been published[27] on the oxidisability of nickel(II) chelates formed with dihydric *o*-phenols and their mono- and di-thio-analogues in acetone at a platinum electrode. In terms of the ease of their oxidation, these chelates can be arranged in the following sequence: $NiS_4 > NiO_2S_2 > NiO_4$. The irreversible one-electron oxidation in methylene chloride of complexes of the type $Ir(CO)XL_2$, where X = halide anion and L = tertiary phosphine, terminates with the formation of a dimer having a metal–metal bond, in which iridium is in the 2+ oxidation state[85].

IV. THE ROLE OF THE NATURE OF THE METAL AND THE STRUCTURE OF THE LIGAND IN THE MECHANISM OF THE ELECTROCHEMICAL REDUCTION OF CHELATES

The results of the electrochemical study of the coordination compounds of *d* elements with organic ligands in non-aqueous solvents make it possible to put forward general considerations concerning the influence of the nature of the central atom and the ligand on the nature of the electrode reactions. Depending on the electronic configuration of the complex-forming ion and the type of ligand, chelates are reduced in one or several stages. In terms of the nature of the first stage, electrochemical processes can be conventionally divided into two large groups. The metal chelates of the first group, which are of the inner complex type, undergo reversible reduction at the m.d.e. A slow electron transfer in the electrochemical stage proper is more characteristic of the second group. The conventional nature of this subdivision is due to the fact that in many instances, for example, with increased concentration of the depolariser, the process is complicated by the adsorption of the latter on the m.d.e. and becomes irreversible. For certain inner complexes, charge transfer is complicated by the subsequent chemical deactivation of the primary electron transfer product. The chelates of the second group are reduced irreversibly regardless of the duration of electrolysis in the course of the recording of the polarisation curve.

Among the electrochemical reactions of chelates in the first group, reversible one-electron processes, which can be regarded as purely electron transfer reactions, are of greatest interest. With rare exceptions, they are characteristic of metal chelates (including inner complexes), with unfilled *d* shells. In multistage reduction, with the transfer of one electron in each stage, intermediates are formed in which the central atom is in a formally low oxidation state. In such cases the electrochemical process can be represented as electron transfer to the lowest unoccupied molecular orbital; $E_{1/2}$ is a thermodynamic quantity and reflects the energy level of this orbital of the complex. The reaction centre to which an electron is transferred is delocalised and embraces a group of atoms with a common unoccupied molecular orbital, including the metal atom. When the electron occupies the lowest vacant molecular orbital, the activation barrier is apparently comparatively low[86].

In those cases where a rigorous correlation is observed between the half-wave potential and the $\Sigma\sigma$ of the substituents (the Hammett or Taft constants), the latter must be regarded as a consequence of the different sensitivities of the lowest unoccupied molecular orbital to the influence of substituents. The deviation of the values of $E_{1/2}$ from those predicted by the regression equation can have different causes: adsorbability of the components of the electrochemical reaction on the electrode surface, the influence of the subsequent chemical reaction, for example, with the solvent or impurities in the latter, etc. In this case the half-wave potential loses its rigorous thermodynamic significance, because it reflects not only the energy level of the lowest unoccupied molecular orbital of the complex, but also the influence of the subsequent chemical stage. The contribution of adsorption to the electrode process, which complicates the correlations, is particularly notable for complexes of sulphur-containing ligands.

The values of $E_{1/2}$ for reversible uncomplicated stages can be correlated with photoelectron spectroscopic data characterising the electron binding energies. Such correlations make it possible to predict the properties of hitherto unknown complexes.

The problem of the oxidation state of the central atom in the intermediate species formed is fairly complex. Quantum-chemical calculations of the populations of the atomic orbitals and of the degree of their overlap, which make it possible to discover the composition of the orbital to which an electron is transferred in the electrochemical stage proper as well as the most probable distribution of electron density in the one-electron transfer product, might be very useful. Such calculations have been made for certain types of coordination compounds. They showed, for example, that the molecular orbital to which an electron is transferred in the reduction of ruthenium(III) tris-β-diketonates is of the ligand type. This result implies that the contribution of the metallic t_{2g} (or e_a) orbital is much smaller than the contribution of the $\pi(\sigma+\pi)$ orbitals of the ligand to the common unoccupied molecular orbital of the complex. This is consistent with the considerable influence of the nature of the substituents on the ease of reduction[24]. However, for the majority of metal coordination compounds with different donor atoms, quantum-chemical data are not as yet available.

The unpaired electron in the one-electron reduction product can occupy one of the vacant *d* orbitals of the metal, so that the oxidation state of the latter is determined by the charge of the complex species. Its stability depends to a large extent on the π-acceptor properties of the ligand. π-Acceptor ligands are known to decrease the energy of the orbitals localised predominantly at the central atom and to increase the strength of the metal–ligand bond via the reverse dative bonding mechanism. This explains the fairly high stability of transition metal complexes of bipyridyl and terpyridyl with the central atom in a low oxidation state, which are formed in electrochemical reduction in non-aqueous media.

Analysis of literature data shows that the stabilisation of complexes with metals in low oxidation states depends on the nature of the ligands, the nature of their donor atoms, the number of rings formed, and the nature of the metal. In addition, account must be taken of the aromatic properties of the chelate rings formed. The formation of species with the metal in the 1+ oxidation state in the reduction of tris-complexes of iron(II) with aliphatic di-imines of the type $H_3C-N=C(R)-C(R)=N-CH_3$, where R = H or CH_3,[86] can be explained by the fact that the chelate units in these complexes and in the bipyridyl complexes are similar.

It is of interest that the apparent standard electron transfer rate constants lie in the narrow range of values $1\times10^{-2} - 2.5\times10^{-2}$ cm s^{-1} for a large group of metal chelates (thio- and bisthio-semicarbazones, dithiocarbamates, and complexes with *o*,*o'*-dihydroxyazo-compounds). The probable cause of this may be the similarity of the transition states in the charge-transfer reaction and of the factors which determine the magnitude of the energy barrier[87]. The dependence of k_S on the electronic configuration of the reacting species has been discussed[61–63]. If the metal orbital, for example t_{2g}, delocalised over the molecule and involved in the formation of an $M \rightarrow L\,\pi$ bond (in chelates with bipyridyl, terpyridyl[57,62], and the di-imines mentioned above[86]) makes the main contributions to the molecular orbital to which an electron is transferred, then the change in the geometry of the species formed as a result of the latter process can prove to be insignificant compared with the change in the geometry of the initial depolariser molecule. In other words, if the electrolysis product differs from the depolariser by not more than one electron, then the molecules with the metal in both oxidation states can have approximately the same configuration.

In this case the rate of electron transfer is fairly high, and, conversely, the activation energy for the reverse process is relatively small. An electron may be transferred to a molecular orbital made up of atomic orbitals of another type, for example, e_g, involved in the formation of an M–Lσ bond; under these conditions, electron transfer leads to appreciable changes of the length of the M–L bonds, and hence in the geometry of the molecules of the reduction products. Such a process requires a greater activation energy and the rate of charge transfer is therefore comparatively low. In general, k_S, determined experimentally by relaxation electrochemical methods, is frequently much lower than the theoretical value[62]. Apart from the factors mentioned above, k_S can be influenced by the range of potentials in which the complexes are reduced and by the charge of the complex species. Thus it has been concluded[88] that the formal charge has a significant influence on the rate of electron transfer (the heterogeneity of the process) and that the reorganisation of the solvent can play an important role. We may recall the Vlček rule, according to which the reduction potential is more negative the greater the degree of localisation of the orbital to which the first electron is transferred[89]. This is consistent with the data for bipyridyl complexes[62,90]. However, it is still unknown whether this conclusion is valid for metal chelates with sulphur-containing ligands[27].

Slow charge transfer in the electrochemical stage proper is characteristic of coordination compounds of cobalt, nickel, and copper and certain other metals with thio- and seleno-semicarbazones, formed without substitution of hydrogen atoms (the second group of complexes). They have the structure of chelates but the latter does not include cyclic $(pd)\pi$ systems, typical for inner complexes, which ensure the delocalisation of electrons via a d-orbital centre. Since chelates in this group are charged, they are highly solvated in DMF and similar solvents. Part of the coordination capacity of the metal can be consumed in the interaction with the solvent, particularly when the ligands have polar groups. The formation of a solvation shell hinders electron transfer to the depolariser, i.e. gives rise to an overvoltage. Thus, on passing to solvents with high donor numbers and high dielectric constants, the reversibility of the reduction diminishes[3] and $E_{1/2}$ undergoes a cathodic shift[91].

This review describes the results of some of the studies on the coordination compounds of metals and similar systems by modern electrochemical methods, which are being prosecuted at the present time[92–94]. Presumably the conclusions and generalisations concerning electrochemical properties of metal chelates with organic ligands having comparatively simple structures will in future prove useful in the study of complexes with more complex ligands, whose oxidation-reduction reactions simulate the biological functions of natural products (vitamins, enzymes, etc.) belonging to the class of coordination compounds. The electrochemical processes involving many organic physiologically active compounds are known to occur at fairly high potentials, which are not attainable in biological systems. It is logical to suppose that the physiological activity of many of these compounds may be due to complexes of the compound with microelements in living tissues and not to the initial compound itself. The redox properties of such complexes can differ significantly from those of the organic compound and their oxidation-reduction potentials are usually much lower and are within the scale of potentials characteristic of the living cell[95]. Finally, the study of the properties of chelates makes it possible to select conditions for the electrosynthesis of compounds with valuable properties, including catalytic activity in homogeneous processes[96,97]. This should be encouraged by the development of research into the reactions of chelates at electrodes made of materials of different types[98,100] and a deeper investigation into the essential features of the processes involving coordination compounds, which is impossible without further comprehensive study of their structures by various methods, including electrochemical methods.

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Dissociative Ionisation of Nitro-derivatives of Arenes and Heterocyclic Compounds

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The mass-spectrometric behaviour of nitro-derivatives of aromatic and heterocyclic compounds is examined. Attention is concentrated on the influence of the relative positions of nitro- and other functional groups on the mode of decomposition in the mass-spectrometry of positive and negative ions.
The bibliography includes 92 references.

CONTENTS

I. Introduction 463
II. Nitroarenes 463
III. Nitro-derivatives of heterocyclic compounds 468

I. INTRODUCTION

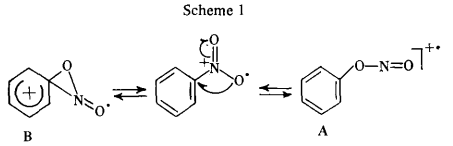
Numerous mass-spectrometric studies have been devoted to analysing the behaviour of various classes of organic compounds on electron impact. However, it has now become necessary to examine various classes of compounds containing functional groups which have a decisive influence on the mode of fragmentation. The types of decomposition associated with different positions of the functional groups in the aromatic or heterocyclic ring are particularly important. One of the most important and frequently encountered functional groups in organic compounds is the nitro-group, whose presence frequently leads to specific modes of decomposition of molecular ions. There are no reviews in the literature of studies on these problems; the aim of the present review is to fill this gap. It includes studies published up to the end of 1975.

II. NITROARENES

The first studies on the mass-spectrometric behaviour of mono- and polynitrobenzenes [1-7] established the occurrence in their dissociative ionisation processes of three main characteristic pathways: the formation of the ions $(M - O)^+$, $(M - NO)^+$, and $(M - NO_2)^+$. However, under these conditions the probability of the first process was very low and the intensity of the corresponding peak in the mass spectrum did not usually exceed 1-2% (of the maximum peak).

It has been suggested [1] that the molecular ion derived from nitro-compounds partly rearranges with formation of aryl nitrite ions A before dissociation:

Scheme 1



B A

However, according to other workers [2], the rearranged ion has the *spiro*-structure B.

The occurrence of the isomerisation of the nitro-group was subsequently confirmed and accepted all by investigators of the mass spectra of nitro-derivatives of aromatic and heterocyclic compounds.

Having compared the mass spectra of all the isomeric dinitrobenzenes (see Table), Beynon et al. [1] and Fields and Meyerson [3] concluded that the modes of decomposition of these compounds and other nitroarenes are similar. It was noted that the mass-spectra of *meta*- and *para*-isomers are very similar, but differ markedly from that of the *ortho*-isomer [1,4]. Thus the intensity of the M^+ peak is appreciably lower in the mass spectrum of the *ortho*-isomer, which reflects its lower stability. In this connection one should note that the mass spectrum of *ortho*-dinitrobenzene exhibits [8] the peak of the $(M - O_3)^+$ ion (mass 120), to which the authors attributed the structure of benzo[3,4]-1,2,5-oxadiazole and showed that this compound is indeed formed also in the pyrolysis of *o*-dinitrobenzene at 650°C.

The peak intensities of the characteristic ions in the mass spectra of isomeric dinitrobenzenes (as percentages of the total ionic current). [1,4]

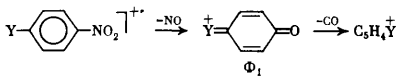
Ion	Position of nitro-group		
	ortho-	*para*-	*meta*-
M^+	6.98	11.00	10.30
$(M—O)^+$	0.24	0.63	0.57
$(M—NO)^+$	0.07	0.21	0.34
$(M—NO_2)^+$	0.41	4.76	4.12
$(M—NO—NO)^+$	0.03	0.04	0.09
$(M—NO—NO_2)^+$	1.66	5.82	3.64
$(M—NO_2—NO_2)^+$	3.84	11.20	9.18
$(M—NO_2—HNO_2)^+$	2.03	10.80	11.30
NO^+	26.70	17.20	21.30

The nature of the decomposition of the negative molecular ions of mono- and poly-nitrobenzenes [9,10] does not differ fundamentally from that of the processes described above, although the fragmentation of such ions is more selective.

Meyerson et al. [5] used the defocussing method and high-resolution mass spectrometry for a detailed study of 1,3,5-trinitrobenzene. For 23 ions, they observed 96 corresponding metastable peaks, which enabled them to devise a very complex scheme relating the precursor ions to daughter ions; the authors reduced the main "chains" of molecular ion decomposition processes to six pathways, resembling the pathways in the fragmentation

of dinitrobenzene (see Table). It is very remarkable that in the first stage the elimination of NO_2 plays the main role. In contrast to mono- and di-nitrobenzenes[1,6,7], the abstraction of O from M^+ is not observed for trinitrobenzene. It is also of interest to note that the mass spectrum of nitrosobenzene contains the peak of the $(M - N)^+$ ion with a mass of 93, but the authors did not express a view concerning the process involving its formation[11].

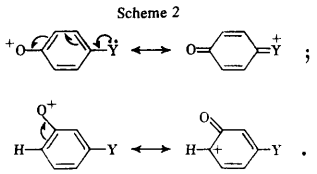
The studies of Bursey and McLafferty[2] showed that the abstraction of NO from M^+ for certain substituted aromatic nitro-compounds is associated with the appearance of peaks with a flat top due to metastable ions, which indicates the liberation of kinetic energy. The generation of a metastable peak associated with the elimination of NO is characteristic of all 27 compounds investigated, but the formation of the peaks with a flat top was noted for only five of them, the amount of energy liberated being in the range 0.38–0.84 eV. The liberation of kinetic energy is associated with the following type of decomposition of the system:



Φ_1

in which the ion Φ_1 formed undergoes resonance stabilisation by the electron donor substituent in the *ortho*- or *para*- (but not *meta*-) position[2]:

Scheme 2

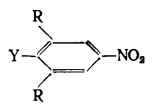


Indeed the liberation of kinetic energy was observed only for *para*-substituted nitrobenzenes and only for substituents with $\sigma_Y > 0.40$.

A study of the dissociative ionisation of mono- and di-nitro-phenyl sulphones[12,13] also showed that the probability of the nitro–nitrite isomerisation of M^+ is determined by the position of the nitro-group in the molecule. It occurs most readily when one or both nitro-groups are in the *para*-positions relative to the sulphone group. We need only note that a competing S–O migration of the aryl group, leading to the formation of aryl esters of arene sulphinic acids, is observed in the decomposition of the above sulphones.[14]

In full agreement with the above considerations, the liberation of the greatest amount of kinetic energy was noted in the mass spectra of the negative ions[9] of isomeric dinitrobenzenes on formation of the ion $(M - NO)^+$ (0.89 eV) from the *para*-isomer, the value for the *meta*-isomer being significantly smaller (0.36 eV). As was also to be expected, the intensity of the $(M - NO)^+$ ions in the mass spectra of negative ions (in full contrast to the mass-spectra of positive ions) was directly proportional to the electron-accepting properties of the substituent in the *para*-position[10].

Many other studies on the mass spectra of both negative[15,16] and positive[17-20] ions support the maintenance of the non-identity of the positions in the series of nitroarenes in both the first and subsequent decomposition stages. In particular, having analysed the mass spectra of three series of sterically hindered *para*-substituted nitroarenes having the general formula



Y=HO, CH_3O, H_2N, or $(CH_3)_2N$; R = H, Cl, or Br.

Bursey[21] showed that the displacement of the substituent Y from the plane of the benzene ring, which promotes a decrease of the p–π conjugation between them, reduces the intensity of the peak of the $(M - NO)^+$ ion. These data also support the view that substituents influence the decomposition of nitroarenes.

The results of an earlier study[22], dealing with the ionisation potentials (IP) and appearance potentials (AP) of ions arising, apparently, in the competing reactions involving the decomposition of $M^{+\cdot}$ with formation of the $(M - NO_2)^+$ ion and the rearrangement of the molecular ion with formation of the (M – NO) fragments in the series of *meta*- and *para*-substituted nitrobenzenes (with the substituents Y = NH_2, OH, OCH_3, CH_3, H, Cl, Br, CN, or NO_2), lead to the same conclusion. The differences between the IP and AP, which represent the approximate activation energies (ϵ_0) for the decomposition of the molecular ion leading to the formation of the $(M - NO_2)^+$ fragment are the same for the *meta*- and *para*-positions, whereas in the formation of the $(M - NO)^+$ ion they are different. Finally, having compared the shapes of the peaks due to metastable ions in the mass spectra of *para*-substituted anisoles and nitrobenzenes, Davies and Williams[23] concluded that the structures of the $(M - CH_3)^+$ ions of anisoles and the $(M - NO)^+$ ions (Φ_1) of nitrobenzenes are identical, which suggests that there is no randomisation in these processes.

Nevertheless there have been a number of studies in which the possibility of the randomisation of hydrogen in the fragmentation of benzene[24] and its derivatives[11,25] was demonstrated fairly convincingly. It has also been established[26] that, in the mass spectrum of 4-nitroaniline containing ^{13}C in the 1-position, the $(M - NO)^+$ ion loses one-sixth of the labelled carbon in the form of CO, which indicates a randomisation process involving at least this ion. However, later these data were disproved[27].

Thus, there is as yet no unanimous view concerning the retention or non-retention of the identity of the position of the substituent in the molecular ions of nitroarenes.

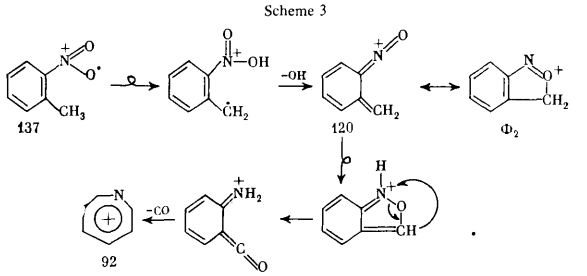
Comparison of the mass spectra of the isomeric nitrotoluenes leads to the conclusion that the decomposition reactions of their *meta*- and *para*-isomers are very similar to the decomposition of nitrobenzene[1]. Thus both isomers are characterised by intense peaks due to the molecular ion (>70% of the maximum), the intensity being comparable to the intensity of the peak of the $M^{+\cdot}$ radical-ion derived from nitrobenzene (49%). For all three compounds, the maximum peak in the mass spectrum corresponds to the $(M - NO_2)^+$ ions, the intensity of the peaks due to the $(M - NO)^+$ ions is 10%, while the peak of the $(M - O)^+$ ions amounts to 1–2% of the maximum peak.

At the same time the mass spectrum of *o*-nitrotoluene exhibits significant differences. The peak of the M^+ ion amounts to only 25%, there is no peak due to $(M - O)^+$ ions, and the maximum peak corresponds to ions with a mass of 120, which are absent from the mass spectra of the *meta*- and *para*-isomers.

The use of high-resolution mass spectrometry and of data for metastable processes, enabled Beynon et al.[1] to establish unambiguously that these ions can have the elemental composition C_7H_6NO, i.e. correspond to the $(M - OH)^+$ ions with the probable structure Φ_2. Subsequently ions having this mass lose 28 atomic mass units (a.m.u.) (CO) and are converted into ions with a mass of 92, which probably have the structure of the azatropylium ion, because the last stage in its decomposition involves the elimination of hydrocyanic acid.

Thus the characteristic pathways leading to the fragmentation of *o*-nitrotoluene reduce to three consecutive processes†:

Scheme 3



Only the $(M - NO)^+$ and $(M - NO_2)^+$ ions were observed in the mass spectra of *m*- and *p*-nitrotoluenes. The $(M - OH)^+$ ions were characteristic of both nitro-*p*-xylene and of polynitrotoluenes[1]. Similar processes are characteristic also of the mass spectra of the negative ions of nitrotoluene or analogous compounds[10,28], whereas the ions $[(M + H) - OH_2]^+$ were observed in the mass spectrum of trinitrotoluene obtained by chemical ionisation[29].

When one of the hydrogen atoms of the methyl group in *o*-nitrotoluene is replaced by an amino-group, the $(M - OH)^+$ ion subsequently loses NO and not CO, which indicates its non-cyclic structure[30].

The formation of the $(M - OH)^+$ ions is observed also in the series of isomeric nitroanilines[1,31]. Thus, whereas the mass-spectrum of *o*-nitroaniline contains the peak of the $(M - OH)^+$ ion (although it is less intense than in the mass spectrum of *o*-nitrotoluene), such a peak is not characteristic of the *meta*- and *para*-isomers. The same process, involving the loss of an OH group, is also typical for the mass spectra of negative ions derived from *o*-nitrotrifluoroacetanilides and it has also been shown that the hydrogen ion is eliminated from the NH group[32].

On the basis of the foregoing considerations, one can conclude that the early studies on the mass spectra of nitroarenes already gave rise to the necessity for a detailed investigation of the influence of the *ortho*-effect[33,34] on dissociative ionisation. This influence applies particularly when the substituent in the *ortho*-position relative to the nitro-group contains a hydrogen atom, which makes possible the abstraction of the hydroxy-group from M^+.[35] Such elimination of OH does not occur for the *meta*- and *para*-isomers.

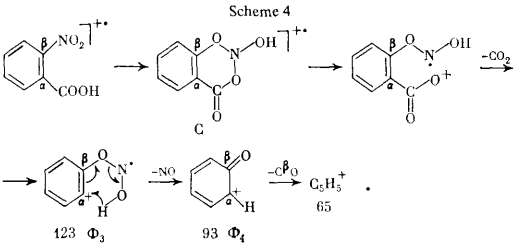
†Here and henceforth the number under the formula of the ion represents the corresponding value of *m/e*, the number in round brackets represents the intensity of the peak of the given ion as a percentage of the maximum peak in the spectrum, and the number in square brackets represents the intensity of the peak of the given ion as a percentage of the total ionic current.

It has been suggested[1] that this process proceeds via a six-membered transition state with migration of a hydrogen atom to an oxygen atom of the nitro-group and the OH group is eliminated from the non-rearranged M^+ ion and not from the ion in the nitrite form.

Williams and coworkers[36] investigated the *ortho*-effect in the mass spectra of certain nitroarenes, where the substituent in the *ortho*-position contained oxygen. All the decomposition mechanisms involved interaction between the *ortho*-groups; however, this was accompanied by unexpected effects, which may be associated with the presence of impurities or with thermolysis of the nitro-compounds.

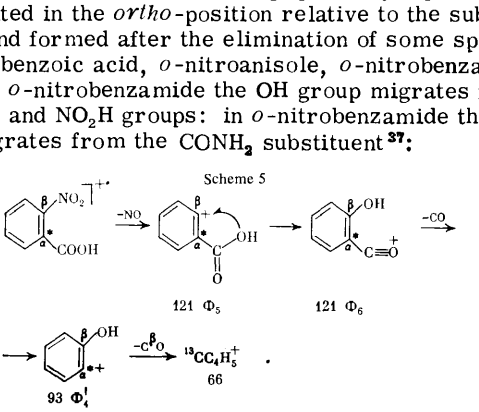
Benoit and Holmes[37] examined this problem in relation to the dissociative ionisation of *o*-nitrobenzoic acid, *o*-nitroanisole, *o*-nitrobenzamide, *o*-nitrobenzyl alcohol, and *o*-nitrobenzaldehyde. Some of the compounds investigated were labelled with deuterium, while in other cases the ^{18}O label was used. It was concluded that there are two types of *ortho*-effects. The first was already noted above in connection with the migration of a hydrogen atom from one substituent to another. In the compounds under consideration such migration to an oxygen atom of the nitro-group is usually accompanied by a complex rearrangement and leads to the elimination of a neutral species (a molecule). Such a process proceeds as a rule with the intermediate formation of a five- or six-membered cyclic structure. In the case of *o*-nitrobenzoic acid, *o*-nitroanisole, and *o*-nitrobenzaldehyde the formation of a cyclic intermediate structure is accompanied by the nitro–nitrite isomerisation (Scheme 4). The same processes characterise also the mass spectra of negative ions[10,38].

Scheme 4



The second type of *ortho*-effect is associated with the migration of an atom or group of atoms from the substituent to a vacant site in the ring (probably a positive hole) located in the *ortho*-position relative to the substituent and formed after the elimination of some species. In *o*-nitrobenzoic acid, *o*-nitroanisole, *o*-nitrobenzaldehyde, and *o*-nitrobenzamide the OH group migrates from the COOH and NO_2H groups: in *o*-nitrobenzamide the NH_2 group migrates from the $CONH_2$ substituent[37]:

Scheme 5



Here the asterisk denotes a ^{13}C atom.

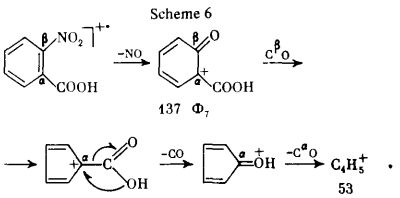
Many efforts have been made to elucidate the mechanism and the pathways leading to the formation and decomposition of the ion with a mass of 93 in the mass

spectrum of *o*-nitrobenzoic acid. Benoit and Holmes [37] proposed two alternative mechanisms, the first of which (Scheme 4) presupposes the migration of acid hydrogen to the isomerised nitro-group with formation of a cyclic structure C, which, having eliminated CO_2, gives rise to the ion Φ_3. The latter next ejects an NO molecule and forms an ion with a mass of 93 (Φ_4). The loss of CO by the latter leads to the formation of the hydrocarbon ion $C_5H_5^+$ (with a mass of 65). The second probable pathway leading to the formation of an ion with a mass of 93 presupposes the ejection of the nitro-group (the Φ_5 ion), the migration of the hydroxy-group (Φ_6), and the loss of CO (the Φ_4 ion) (see Scheme 5).

Having investigated the mass spectra of *o*-nitrobenzoic acid containing ^{13}C in the 1-position using ionising electron energies of 17 and 15 eV, Djerassi and coworkers [39] found that the label is not lost up to the ion with a mass of 65. However, analysis of the mass spectrum of the compound containing ^{18}O in the hydroxy-group showed that the label is not lost on formation of the ion Φ_5, but the ion Φ_4 contains only part of the label. Thus both mechanisms (Schemes 4 and 5) operate.

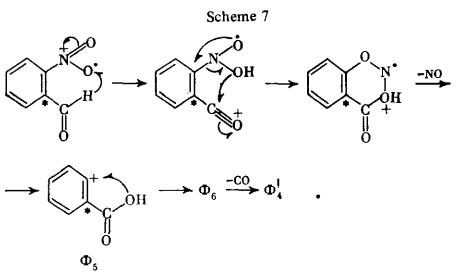
Benoit and Holmes [37] proposed also a third mechanism for the dissociative ionisation of the molecular ion of *o*-nitrobenzoic acid (Scheme 6), which is also consistent with Djerassi's data [39]. However, the ions $\Phi_7 - \Phi_{10}$ formed via this pathway give rise to much less intense peaks than the ions $\Phi_2 - \Phi_6$, so that one can assume that the above pathway does not play a significant role in the overall decomposition mechanism:

Scheme 6



The migration of hydrogen to the oxygen of the nitro-group is observed also in the mass spectrum of *o*-nitrobenzaldehyde in which the $(M - NO)^+$ ion next loses CO and the process proceeds via Scheme 7, proved by Djerassi and coworkers [39] by analysing the mass spectrum of the compound containing ^{13}C in the formal group:

Scheme 7

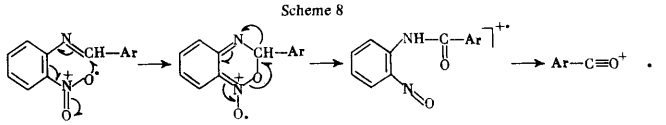


Here the asterisk denotes a ^{13}C atom. There is a possibility of the migration not only of a hydrogen atom but also of an amino-group to an oxygen atom of a neighbouring nitro-group [40], while in the mass spectra of negative ions even the phenyl group can migrate [41], as has been shown for the isomeric phenyl nitrosalicylates and *o*-nitrophenyl ether [42].

The replacement of oxygen by nitrogen in *o*-nitrobenzaldehyde does not change significantly the primary decomposition in both positive [43] and negative [44] mass spectra.

However, there is no $(M - OH)^+$ ion in the mass spectra of the benzylidene derivatives of *o*-nitroaniline, [42] but the transfer of the oxygen of the nitro-group to the methylidyne carbon atom with the simultaneous migration of hydrogen and the formation of the $(Ar - CO)^+$ ion are observed:

Scheme 8



A similar transfer of the oxygen of the nitro-group to the C=C double bond has been observed for esters of α-benzylidene-*o*-nitrobenzoylamino acids [45]. The same type of migration of an oxygen atom of the nitro-group to a neighbouring double bond [(C=C) or C=N] was noted by investigators [46] who studied the dissociative ionisation of 40 compounds comprising nitrophenylhydrazones, aromatic aldehydes and ketones, nitrostilbenes, and nitrobenzylideneacetophenones.

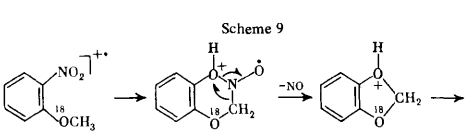
An analogous transfer of an oxygen atom from the nitro-group has been observed in the mass spectrum of *o*-nitrostyrene [there are intense peaks due to the $(M - CO)$, $(M - CHO)$, and $(M - CH_2O)$ ions]. [47] Finally, the migration of an oxygen atom of the nitro-group to a sulphur atom with subsequent elimination of the *p*-tolyl sulphoxide residue has been observed in the molecular ion derived from *p*-tolyl *o*-nitrothiobenzoate. [48]

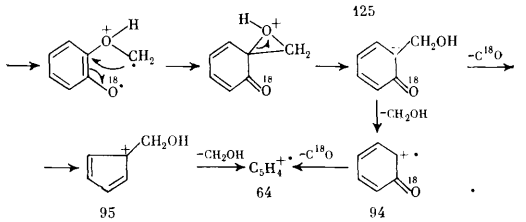
The study of the behaviour of *o*-nitroanisole under electron impact showed [37] that the main primary process in the decomposition of its molecular ion is the loss of 30 a.m.u. with formation of an ion having a mass of 123. Using high-resolution mass spectra it was established that the loss of CH_2O proceeds to an extent that 80% and that of NO only to an extent of 20%.

Analysis of the mass spectrum of *o*-nitroanisole containing ^{18}O in the methoxy-group established unexpectedly [39] that the elimination of CH_2O does not entail the loss of labelled oxygen. Schemes 9 and 10 explain all the experimental facts and include, as in the previous instance, the migration of the OH group to a vacant site at a ring carbon atom. It must be emphasised that the thermal decomposition processes involving *o*-nitroanisole proceed with loss of HNO and HNO_2. [49]

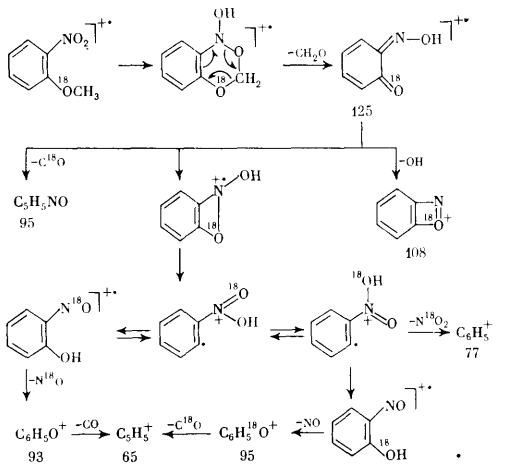
Hydrogen can also migrate to the nitro-group from the *peri*-position. Thus the mass spectra of nitro-compounds exhibiting *peri*- and *ortho*-effects have been examined [36] and the authors observed a number of analogies in the behaviour of nitro-compounds in photochemical reactions and under electron impact. The study of the decomposition of 1-nitronaphthalene showed [36] that the mass spectrum contains the ion Φ_{12} [$(M - 28)^+$] with a mass of 145, which was identified as the $(M - CO)^+$ ion on the basis of high-resolution mass spectrometric data. The appearance of such ions was not noted in the mass spectra of nitrobenzenes.

Scheme 9



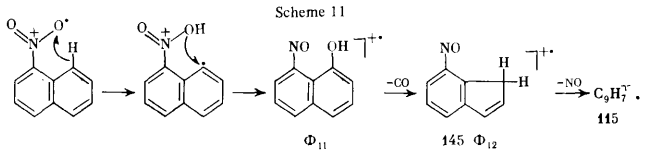


Scheme 10



Its formation is most probably caused by the formation of a new bond between the $C_{(8)}$ *peri*-carbon atom and an oxygen atom of the nitro-group, which enabled the authors to propose a mechanism for the elimination of CO:

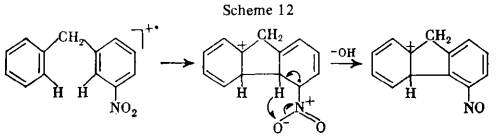
Scheme 11



According to this scheme, there is initially the migration of a hydrogen atom in the $M^{+\cdot}$ species derived from nitronaphthalene and then the migration of the hydroxy-group. The ion Φ_{11} with a nitrosophenol structure formed in this process can eliminate CO, similarly to the process observed for phenols[50]. The subsequent decomposition of the ion Φ_{12} is confirmed by the proposed mechanism. It is important to emphasise that 1,5-dinitronaphthalene does not eliminate CO under electron impact. An analogous reaction has been observed[51] in the photolysis of 6-nitrocholesteryl acetate.

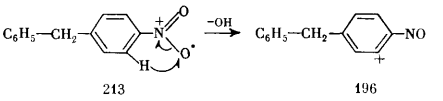
Similar processes involving the migration of an aromatic hydrogen atom in a neighbouring aryl group have also been discovered[52] in the mass spectra of the isomeric *o*-, *m*-, and *p*-benzylnitrobenzenes. It was established that the $(M - OH)^+$ ion, the formation of which can be readily accounted for in the case of the *ortho*-isomer, is observed also in the mass spectra of other isomers. The study of the dissociative ionisation of the deuterium-labelled compounds made it possible to show that the process involving *m*-benzylnitrobenzenes proceeds via the scheme

Scheme 12



In the *para*-isomer, where the $(M - OH)^+$ ion is formed with a low probability, hydrogen also migrates, but from the CH_3 group and not the *ortho*-position:

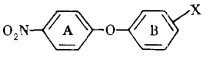
Scheme 13



It was later established that the formation of the $(M - OH)$ and even $(M - 2\ OH)$ (in the case of *ortho*-isomers) ions is characteristic of the mass spectrometric behaviour of nitrodiphenylamines.[53] Beynon and coworkers observed the peaks of the $(M - NO)$ ions also in the mass spectra of esters, amides, thioamides, hydrazides, and iminoesters of *p*- and *m*-nitrobenzoic acids. They explained their formation by a multistage migration of a hydrogen atom from the substituent to an oxygen atom of the nitro-group[54].

The migration of a hydrogen atom from a neighbouring ring was also observed for nitrodiphenyl ethers[53,55] and in the mass spectra of the negative ions of cyclic thioacetyls and of *o*-nitrobenzaldehyde[56].

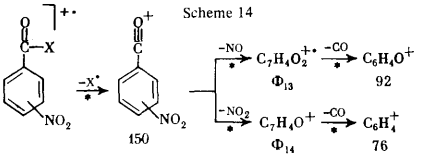
A careful study of the mass-spectrometric behaviour of nitrodiphenyl ethers made it possible[57] to examine the problem of the possible migration of the charge in the excited ion, which has been frequently the subject of a critical discussion in the literature[58,59]. It has been concluded[57] that the nature of the substituent (X) in the B ring plays an important role in the intensity of the fragment ions produced as a result of the nitro–nitrite isomerisation in the ether:



Furthermore, a linear relation has been observed between the intensity of the peaks of the $(M - NO)^+$ ions and the IP, on the one hand, and between the intensity of the peaks of the $(M - NO)^-$ ions and the Hammett constant, on the other. According to the authors[57], the results show that the substituent X in the B rings of the nitroether derivatives investigated has a considerable influence on the electronic state of the A ring and that the electron density in the ion with an odd number of electrons migrates from the electron-depleted A ring to the B ring.

Shapiro and Serum[60] investigated the mass spectra of derivatives of *m*- or *p*-nitrobenzoic acids $O_2NC_6H_4COX$, where X = OCH_3, NH_2, or $NHCH_3$, in order to study the behaviour of the ion with a mass of 150 and an even number of electrons (the nitrobenzoyl cation), formed on elimination of the substituent X and subsequently decomposing via two alternative pathways leading to the formation of the ions Φ_{13} and Φ_{14}, having odd numbers of electrons‡:

Scheme 14



It was shown that the removal of NO from the ion with a mass of 150 for *p*-nitro-compounds proceeds with a much greater probability than for the *m*-isomers.

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‡Here and henceforth an asterisk in the Schemes denotes a process confirmed by the presence of a metastable ion.

Analogous data were obtained in the study of the behaviour of $(M - X)^+$ ions with an even number of electrons and a mass of 136, formed in the dissociative ionisation of the nitrobenzyls *m*- or *p*-$O_2NC_6H_4CH_2X$, where X = Br or OC_6H_5, which decompose subsequently with the elimination of NO and NO_2.[60] It was concluded that, regardless of the pathway leading to the formation of the initial ion and its structure, the ion with a mass of 136 does not have the nitrotropylium structure and its structure is more likely to be of the nitrobenzyl type.

A correlation between the electronic properties of the substituents and the intensity of the peaks of fragment ions as well as their AP in the series of nitroarenes has also been observed in the mass spectra of negative ions, and has been demonstrated convincingly in a series of studies by Bowie and coworkers [15,16,41,42,44]. They established that in carbonyl-containing nitroarenes (nitrobenzophenones, nitrobenzoates, etc.) the negative charge is localised preferentially at the oxygen atom of the carbonyl group. Thus in the series of isomeric nitrobenzophenones the IP and the AP of the $(M - C_6H_5CO)^+$ ions and the heats of their formation are similar to those of the *meta*- and *para*-isomers, but differ from the corresponding values for the *ortho*-isomers.[61]

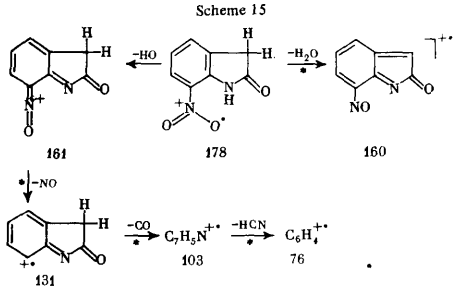
The same workers[61] showed that the mass spectra of negative ions of nitroarenes do not indicate their valence isomerisation or randomisation processes. Similar conclusions were reached also in the analysis of the mass spectra of the negative ions of nitrophthalic anhydride.[62] A considerable similarity between the main dissociative ionisation pathways of this compound in the mass spectra of negative and positive ions[63] and even the mass spectra obtained under the conditions of ion–molecule reactions[64] was noted.

III. NITRODERIVATIVES OF HETEROCYCLIC COMPOUNDS

In contrast to nitroarenes, nitro-derivatives of heterocyclic compounds have been studied to a much lesser extent. The results are difficult to survey owing to the fragmentary nature of the available information about the decomposition reactions of many types of heterocyclic compounds, in the study of which high-resolution mass spectrometry and labelled compounds have been rarely used.

Analysis of the mass spectra of 5-nitro-,[65] 7-nitro-, and 5,7-dinitrooxindoles [66] showed that 7-nitro-oxindole decomposes via the elimination of OH and H_2O from $M^{\ddagger}$ species (Scheme 15), whereas in the fragmentation of 5-nitro-oxindole such ions are not observed and only the $(M - NO)^+$, $(M - HCO)^+$, and $(M - CO)^+$ ions with masses of 148, 149, and 150 are formed:

Scheme 15



The mass spectrum of 5,7-dinitro-oxindole is characterised by decomposition pathways similar to those of 7-nitro-oxindole. Together with the molecular ion, it contains peaks due to the $(M - OH)^+$, $(M - H_2O)^+$, and $(M - OH - NO)^+$ ions with masses of 206, 205, and 176 respectively.

As was to be expected, the introduction of the nitro-group into the molecules of alkylindoles destabilises the molecular ion[67,68]. The primary dissociative ionisation processes are characterised in the first place by the formation of the $(M - NO)^+$ and $(M - NO_2)^+$ ions. Since the nitro–nitrite rearrangement always takes place in the first stage of the decomposition process, the ratio of the peak intensities of these ions reflects qualitatively the statistical weight of the isomerised structure of the molecular ion.

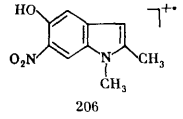
It has been shown[65] that, for an energy of 50 eV, the non-isomerised $M^{\ddagger}$ structures predominate and the fraction of nitrite ions is high only for 1-methyl-3-nitro-indole. The isomerisation proceeds more readily when the nitro-group is in the 6-position and not in the 5-position. The isomerisation of $M^{\ddagger}$ involving the 4- and 7-positions is probably hindered by the stabilisation of the nitro-group as a result of the *peri*-interaction. A decrease of the energy of ionising electrons, which increases the relative probability of rearrangements, increases the probability of the formation of "nitrite" ions approximately by an order of magnitude.

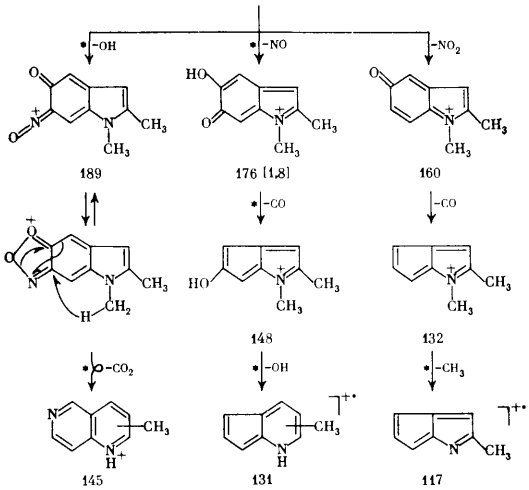
The β-decomposition processes (loss of hydrogen or of an alkyl group), which are typical of methyl indoles[69,70], proceed only in the second decomposition stage in the series of isomeric methylindoles. The presence of a methyl group in the *peri*-position relative to the nitro-group [68] or in the *ortho*-position [71] leads to the appearance of intense $(M - OH)^+$ ions, which permits a reliable identification of the isomers formed in the nitration of methylindoles. Although it is known that the presence of $(M - OH)^+$ ions is also characteristic of the mass spectra of *o*-nitroaniline and its derivatives [1,31], such ions are not observed in the mass spectrum of 7-nitroindole,[68] which is probably associated with the change in the nature of the amino-group in these compounds and the stabilising influence of the fused pyrrole ring.

The introduction of the hydroxy-group into the methyl-nitroindole molecule stabilises somewhat the molecular ion[68,72]. In contrast to oxindoles,[73] significant differences are observed between the mass spectra of the isomeric compounds. Although the stabilities of the $M^{\ddagger}$ species derived from 5-hydroxy-1,2-dimethyl-4-nitroindole and 5-hydroxy-1,2-dimethyl-6-nitroindole are similar, the intensities of certain characteristic ions [for example, $(M - OH - CO_2)^+$, $(M - NO_2 - CO)^+$, and a number of others], typical of *o*-nitrophenol,[1,29] differ by a factor of 2 and more. This indicates the absence of randomisation at the molecular ion stage, probably owing to the presence of the nitro-group. Analogous conclusions were reached in Bowie's study, already mentioned[32].

However, the characteristic pathways leading to the fragmentation of two isomeric nitro-oxindoles, illustrated in Scheme 16 in relation to the 6-nitro-isomer and confirmed by the determination of the elemental compositions of the fragment ions, are fundamentally similar.

Scheme 16

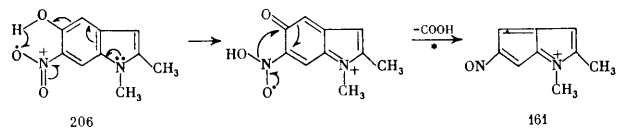




It must be emphasised that, as for methylnitroindoles, the intensity of the $(M - H)^+$ ionic peak in the mass spectra of hydroxymethylnitroindoles does not exceed 0.3–0.4% of the total ion current. This finding suggests a virtually complete suppression of processes typical for the decomposition of alkylindoles, whereas in the mass spectra of hydroxyscatoles peaks of the $(M - H)^+$ and $(M - alkyl)^+$ ions are fairly intense[68].

The presence of a pyrrole ring fused to a benzene ring promotes the stabilisation of intermediate transition states arising in complex rearrangements. Thus, although the principal pathways leading to the dissociative ionisation of nitro-oxindoles,[68,72] containing these functional groups in the 4- and 5-positions or in the 6- and 5-positions, are similar to the fragmentation of *o*-nitrophenol (the successive loss of OH and CO_2 by the moleculer ion or nitro–nitrite rearrangement with elimination of NO), the loss of NO from indole derivatives is three times more intense than in the case of *o*-nitrophenol. Furthermore, the possibility of the elimination of CO_2H from a series of nitro-oxindoles must also be explained by the stabilising influence of the pyrrole ring:

Scheme 17



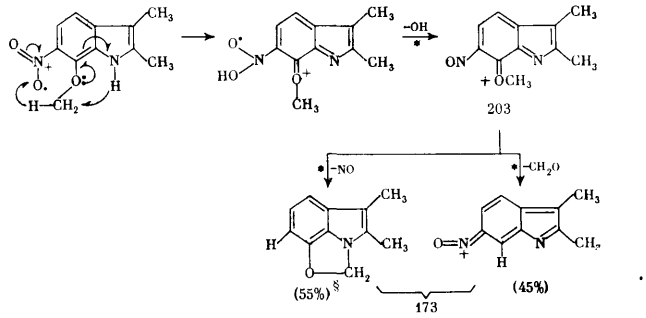
The decomposition pathways of isomeric methoxynitroindoles [68,72] are even more characteristic and differ in many respects from the dissociative ionisation of *o*-nitroanisole. Analysis of the intensities of the characteristic ions in the mass spectra of six isomeric methoxymethylnitroindoles, containing nitro- and methoxy-groups in the *ortho*-positions relative to one another, makes it possible to isolate fragments characteristic solely of the given compound. This permits the identification of each isomer from its mass spectrum. Thus the intense peaks of the $(M - CH_3)^+$ ion (whose intensity in the spectrum of *o*-anisole is low) are characteristic solely of methoxynitroindoles containing the methoxy-group in the 6-position. The rapid loss of the hydroxy-group by the molecular ion is characteristic only of compounds containing the nitro- and methoxy-group in the 6- and 7-positions respectively. However, if there is a methyl group in the 1-position of indole under these conditions, an intense peak of the $(M - NO_2)^+$ ion, which is virtually absent from the mass spectrum of the analogous unsubstituted indole, is observed.

The $(M - OH)^+$ ion mentioned above is completely uncharacteristic of the mass spectra of *o*-nitroanisole and its formation has been attributed[68,72] to the presence in the above structures of the N–H or CH_2–H group in the *peri*-position relative to the methoxy-group, which favours the push–pull transfer of hydrogen to an oxygen atom of the nitro-group (Scheme 18).

When the indole molecule contains simultaneously nitro- and carboxy-groups[71,74], the primary decomposition processes are characterised in the first place by the elimination of an ethoxy-group or an ethanol molecule, which is typical for ethoxycarbonylindoles.[75,76] The elimination or isomerisation and decomposition of the nitro-group take place only in the second stage, i.e. the formation of the primary ions is controlled only by one of the functional groups.

Thus, in contrast to *ortho*-substituted nitroarenes, the *ortho*-substituted nitroindoles decompose via specific channels, which depend on the position of the nitro-group and another functional group relative to the pyrrole nitrogen atom.

Scheme 18



In the series of nitrocarbazoles [77] there are no characteristic pathways which would permit the identification of the isomeric compounds and the most intense fragment ions are $(M - NO)^+$ and $(M - NO_2)^+$. The probability of the nitro–nitrite rearrangement increases by an order of magnitude when the ionisation energy is reduced from 50 to 15 eV. Nevertheless one should note that the ratio of the intensities of the ions $Z = I_{M-MO}/I_{M-NO_2}$ for 3,6-dinitrocarbazole is 1.1, whereas in the case of 3,8-dinitrocarbazole the probability of the elimination of the nitro-group is greater ($Z = 0.72$).

Analogous differences between the values of Z were observed in the series of nitrodibenzofurans,[78] where the 3-nitro-isomer, in which the nitro-group is conjugated with the oxygen atom of the heterocycle, shows the greatest capacity for rearrangement. The same conclusions also follow from the analysis of the mass spectra of a series of isomeric nitroxy-4-oxo-2-chromenes [79] and nitro-substituted N-aryliminopyridyl- and isoquinolinyl-betaines [80] and from the analysis of the mass spectra of negative ions of nitrophenyltriazoles.[81]

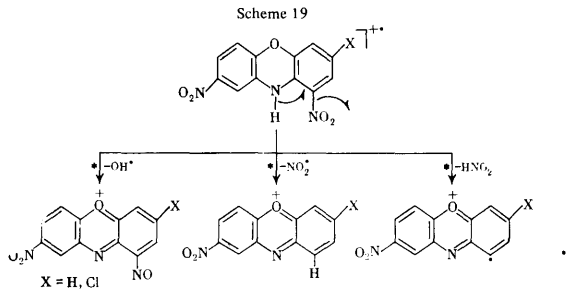
In the dissociative ionisation of nitrophenoxazines and azaphenoxazines [82] the fraction of rearranged ions is very low and the main primary decomposition processes are associated with the elimination of the nitro-group from the molecular ion and, in the case of the 4,6-dinitro-derivative, of a nitrous acid molecule, In the latter case

§The fraction of the ion having the given composition in the ion with $m/e = 173$.

the $(M - OH)^+$ ion, formed with participation of the hydrogen atom of the NH group, is also observed (Scheme 19).

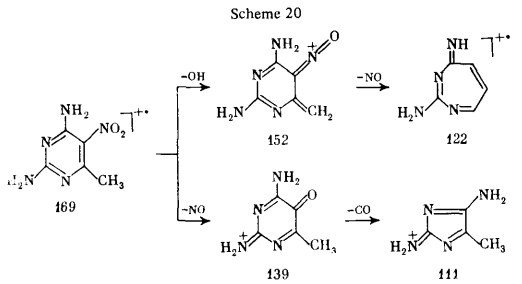
In many instances the occurrence or non-occurrence of the nitro–nitrite rearrangement is associated with the conditions under which the mass spectrum is recorded. Thus the mass spectra of *N*-nitroaminopyridines [83] can be obtained only when they are cautiously introduced into the mass spectrometer by direct injection into the ion source. In this case dissociative ionisation leads to intense peaks of the $(M - NO_2)^+$ ions. On the other hand, the introduction of *N*-nitroaminopyridines via the filling cylinder or using a glass system entails intense pyrolysis, as a result of which the mass spectrum consists of NO_2^+ and NO^+ ions and the products of the dissociative ionisation of aminopyridine, probably formed as a result of an ion–molecule reaction. The mass spectrum of 2-(*N*-methyl-*N*-nitro)aminopyridine, obtained on apparatus with direct injection [into the ion source] shows that the only important decomposition pathway of the molecular ion involves the abstraction of NO_2.

Scheme 19



At the same time the $(M - NO_2)^+$ ions are completely absent from the mass spectra of 4-substituted 2-amino-6-methyl-5-nitropyrimidines [84] and the primary decomposition pathways of these compounds involve the elimination of NO (the main process) or the ejection of OH (as a result of the *ortho*-effect):

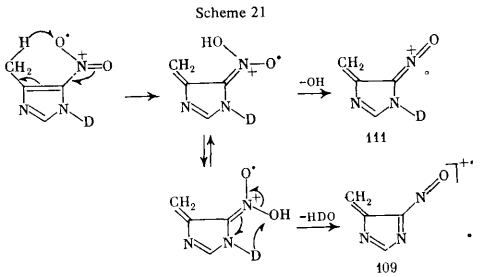
Scheme 20



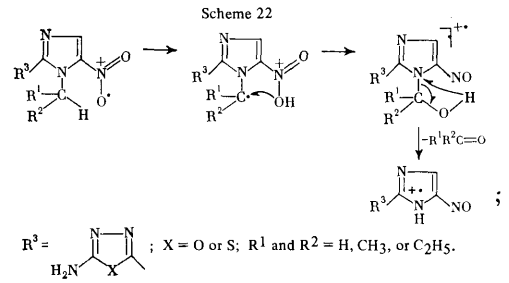
It is of interest that the mass spectrum of this compound also contains the $(M - OH - H_2O)^+$ ion, whose formation is apparently to be accounted for by a double rearrangement of the type found by Lord and Millard [85]. In a study of the mass spectrum of 4(5)-methyl-5(4)-nitroimidazole they observed the so-called "double *ortho*-effect", as a result of which water is eliminated from the molecular ion (Scheme 21), which has been demonstrated by the analysis of the mass spectra of deutero-derivatives.

Van Lear [86] reported an unusual rearrangement associated with the migration of the oxygen of the nitro-group from the nitrogen atom to a carbon atom, which he observed in the dissociative ionisation of a series of 1-alkyl-2-substituted 5-nitroimidazoles. In contrast to the instances described above, the $(M - 30)^+$ ion in the mass spectra of compounds of this type corresponded to the abstraction of CH_2O and not the elimination of NO. In order to account for the findings, a complex mechanism of the rearrangement was proposed, involving double hydrogen transfer and migration of the hydroxy-group (Scheme 22).

Scheme 21

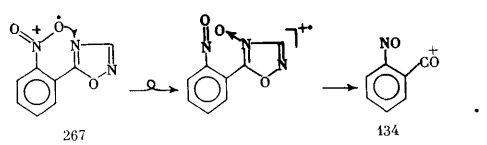


Scheme 22



It must be emphasised that, when the substituents R^3 are alkyl groups, the $(M - 30)^+$ ion is the usual $(M - NO)^+$ ion.

The unusual migration of an oxygen atom of the nitro-group to the nitrogen atom of the heterocyclic ring has also been noted for 5-(*o*-nitrophenyl)-1,2,4-oxadiazole [87]:



Kato and Hirao [88] showed in relation to the mass-spectrometric decomposition of a series of nitrofuryltriazoles that in the case of bisheterocycles the ring containing the nitro-group is mainly cleaved. The kinetic energy liberated as a result of the elimination of the nitroso-group (~0.77–0.81 eV) actually exceeds the value for the analogous processes in the mass spectra of 5-nitro-2-furonitrile and *o*-nitrophenol. [19,20]

Unfortunately, the partial mass spectra of triazoles presented in the literature [88–91] do not permit a sufficiently accurate assessment of the probability of the nitro–nitrite rearrangement when the nitro-group is located in this type of heterocyclic ring. In the case of 10-alkyl-3-nitrophenothiazines and their oxides [92] the $(M - NO)^+$ and $(M - NO_2)^+$ ions were observed solely in the mass spectrum of the 10-methyl derivative without the oxide group.

In the dissociative ionisation of isomeric nitrophenylisoxazoles [93–95] the intensity of the $(M - NO)^+$ ionic peaks is as a rule higher than that of the peaks due to the $(M - NO_2)^+$ ions and a definite correlation has been established between their intensity and the stability of the conjugate cyclic structures where the charge is localised at the oxygen atom.

In the spectra of saturated heterocycles such as isoxazolidines, containing a nitro-group in the 8-position,[96,97] M^+ species are not observed at all and the ions with the maximum mass are $(M - NO_2)^+$.

Thus examination of processes involving the dissociative ionisation of nitro-derivatives of arenes and heterocyclic compounds shows that the occurrence of rearrangements in the molecular ion itself and in the first stages of its decomposition is characteristic of these compounds. The nitro–nitrite rearrangement takes place with a high probability in compounds without any substituents in the *ortho*-position. In this case the probability of the nitro–nitrite rearrangement is related to the electronic influence of the substituents in other positions in the aromatic ring. When an *ortho*-substituent is present, the principal rearrangements are determined by the interaction of the nitro-group with the substituent, which leads to the suppression of the nitro–nitrite rearrangement and the appearance of new decomposition channels characteristic of the given substituent.

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Phosgene in the Chemistry of Organosilicon Compounds

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A systematic account of data concerning the problems of the synthesis of a wide variety of organic and organosilicon derivatives of carbonic acid (chlorocarbonates, carbonates, isocyanates, carbodiimides, acylcarbomoyl chlorides, etc.) by the reaction of phosgene with *N*- and *O*-silyl-substituted amines, amides, diazoles, iminoesters, and ethers derived from alcohols, glycols, etc. is given for the first time.
The bibliography includes 113 references.

CONTENTS

I. Introduction 473
II. Reactions of phosgene with organosilicon compounds having carbon-containing functional groups 473
III. Reactions with compounds having silicon-containing functional groups 475

I. INTRODUCTION

Phosgene is known[1-8] to be very important for preparative and particularly applied organic chemistry. However, there have been only a few scattered studies on the use of phosgene in the chemistry of organosilicon compounds up to 1965. Systematic investigation of the interaction of phosgene with various classes of organosilicon compounds was begun in 1965;[9] more than a hundred publications have now appeared in this field. These studies showed that, as in organic chemistry, $COCl_2$ has led in the chemistry of organosilicon compounds to simple methods for the synthesis of previously unobtainable substances and even whole classes of compounds.

The most novel results have been obtained in the reactions with phosgene of compounds having silicon-containing functional groups, particularly *N*-silylsubstituted derivatives. For example, the use of amines, amides, etc. silylated at the nitrogen atom instead of the corresponding initial organic compounds leads not only to better quantitative results but frequently also better qualitative results. In particular, new preparative pathways leading to the synthesis of lower organic isocyanates, which are difficult to obtain, previously unknown acylcarbamoyl chlorides, and other compounds have been developed.

It must be emphasised that silylation of organic compounds with functional groups, i.e. the replacement by a silyl group (usually Me_3Si) of the mobile hydrogen atom in hydroxy-, amino-, mercapto-, and other groups, can be achieved very simply using readily available reagents[10,11].

II. REACTIONS OF PHOSGENE WITH ORGANOSILICON COMPOUNDS HAVING CARBON-CONTAINING FUNCTIONAL GROUPS

C-Silyl-substituted alcohols, phenols, amines, and mercaptans react, as expected, with carbonic acid chlorides (phosgene, chlorocarbonates) without any fundamental differences from the analogous organic compounds.

1. *C*-SILYL-SUBSTITUTED ALCOHOLS, PHENOLS, AND MERCAPTANS

When $COCl_2$ interacts with organosilicon alcohols, the corresponding chloroformates (chlorocarbonates) are formed in a high yield[9,12-15]:

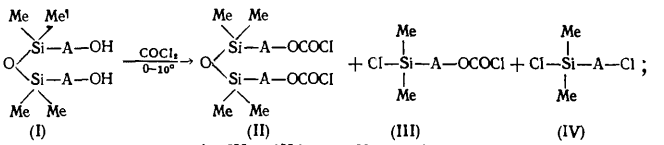
$$R_3Si(CH_2)_nOH \xrightarrow[-HCl]{COCl_2} R_3Si(CH_2)_nOCOCl\ ;\quad R=Alk,\ n=1,2,3.$$

In order to avoid the formation of the diesters of carbonic acids—the organosilicon carbonates $[R_3Si(CH_2)_nO]_2C{=}O$—in a side process, the reaction is carried out at temperatures not exceeding 0–5°C. The position of the hydroxy-group relative to the silicon atom does not influence significantly the yield and mode of reaction.

In contrast to alcohols, silylated mercaptans are more inert in the reaction with phosgene and require the presence of the HCl acceptor for the reaction to be completed[9,12,13,15]:

$$Me_3Si(CH_2)_3SH + COCl_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Me_3Si(CH_2)_3SCOCl\ .$$

The study of the interaction of organosilicon diols of the disiloxane series (I) with phosgene showed that the formation of the desired bischloroformates (II) is accompanied by the cleavage of the siloxane and ether linkages[9,14-20]:

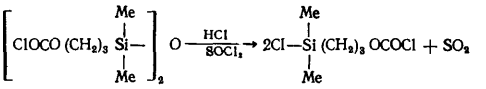


(I) (II) (III) (IV)

A=CH_2, $(CH_2)_3$, or $CH_2OCH_2CH_2$.

It was found that the fraction of side products depends on the type of diol employed[16,21], i.e. on the nature of A.

Special experiments showed[9,14,16] that neither $COCl_2$ nor the bischloroformate (II) are involved directly in the cleavage of the siloxane linkage, while the monochloroformate (III) is formed as a result of the action of HCl, liberated during the reaction, on the disiloxane linkage. For example, the reaction



(IIa) (IIIa)

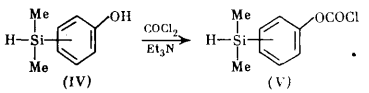
does not occur in the absence of HCl.[9] Like $SOCl_2$, phosgene is an insufficiently powerful reagent for the cleavage of the disoloxane group. For example, when $COCl_2$ is passed for a long time through boiling hexamethyldisiloxane, the rupture of disiloxane linkages does not occur[9,14]. It is also appropriate to mention here that the Si–H bond in hydrosilanes is likewise resistant to the action of $COCl_2$: $SiCl_4$ is formed on contact between $HSiCl_3$ and $COCl_2$ only under very severe conditions (~500°C).[9]

Organosilicon diols containing ether linkages react with $COCl_2$ via a still more complex mechanism[16,21]:

$$[HOCH_2CH_2OCH_2SiMe_2-]_2O \xrightarrow{COCl_2} \underset{65\%}{[ClOCOCH_2CH_2OCH_2SiMe_2-]_2O} + \underset{(17.0\%)}{ClOCOCH_2CH_2OCH_2SiMe_2Cl} + \underset{(2.0\%)}{[ClOCOCH_2SiMe_2-]_2O} + \underset{(1.8\%)}{[ClCH_2SiMe_2-]_2O} + \underset{(3.7\%)}{ClCH_2SiMe_2Cl} + \underset{(3.3\%)}{(ClOCOCH_2-)_2} + \underset{(1.6\%)}{ClCH_2CH_2Cl} .$$

In order to suppress side reactions, it is necessary to remove more completely the hydrogen chloride liberated: diols are treated with phosgene in the absence of solvents capable of retaining HCl, which is displaced by bubbling with dry nitrogen or bound by organic bases[14-16,18,19,22].

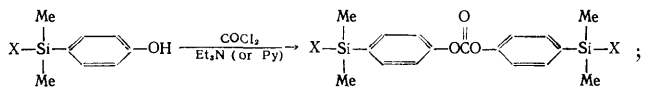
In contrast to aliphatic compounds, organosilicon phenols (IV) are inert in relation to $COCl_2$ at moderate temperatures. In order to avoid the thermal rearrangement of silylphenols to phenoxysilanes[23,24] as well as other side reactions, organosilylphenyl chloroformates (V) were therefore synthesised in the presence of organic bases as HCl acceptors[15-18,21,23,25,26], for example[16,23]:



(IV) (V)

o- and *p*-isomers

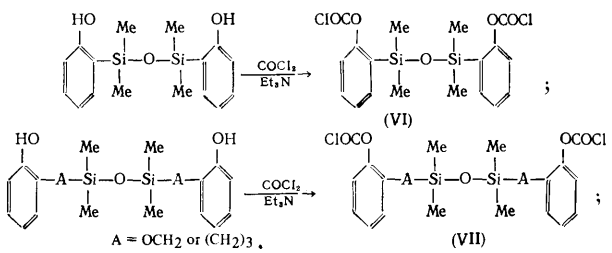
In the presence of an excess of phenol, the corresponding carbonates are formed in a single stage[16,23,26]:



X=H, Cl, or OAlk.

Analogous carbonates were obtained also by the esterification of chlorocarbonates of type (V) by the corresponding silylphenols[16,17,23].

The bischloroformates (VI) and (VII) have been synthesised from bisphenols of the disiloxane series[15-18,21,23,25,26]:



A = OCH_2 or $(CH_2)_3$.

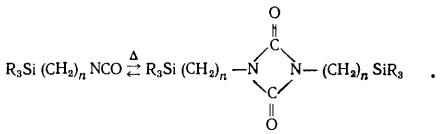
The above bischloroformates are thick transparent compounds soluble in the usual organic solvents. They always distil in an atomosphere of nitrogen without decomposition on heating to 300°C. This finding demonstrates yet again the stability of the Si–O–Si linkages in relation to the action of the chloroformate group even at elevated temperatures. The disiloxane fragment in the above compounds is resistant in the absence of HCl also to the action of $COCl_2$, COF_2, and $SOCl_2$.[16,21,27]

2. *C*-SILYLALKYL(ARYL) AMINES

The reaction of aminoalkylsilanes with phosgene, like the reactions of the *C*-silyl-substituted alcohols, phenols, and mercaptans discussed above, do not show fundamental differences from the reactions of the corresponding purely organic compounds[9,12-15,28]:

$$2R_3Si(CH_2)_nNH_2 + 2COCl_2 \rightarrow 2R_3Si(CH_2)_nNCO + 4HCl ;$$
R = Alk or Ar; $n = 1, 3$.

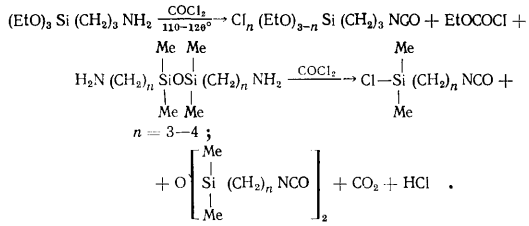
The dimeric compounds (VIII) [9,12] (analogous to the dimers of organosilicon ketens[29]) are formed as side products, which tentatively have the uretidinedione structure and which are in equilibrium with the monomeric form when heated†:



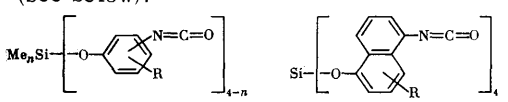
(VIII)

Nevertheless the monomeric isocyanatoalkylsilanes isolated in a pure form are entirely stable. For example, $Me_3Si(CH_2)_3NCO$ does not dimerise on storage or during distillation[9].

When $COCl_2$ interacts with amines containing alkoxy-groups at the silicon atom or siloxane units, the reaction can involve Si–O bonds[9,13,14,31-33]:



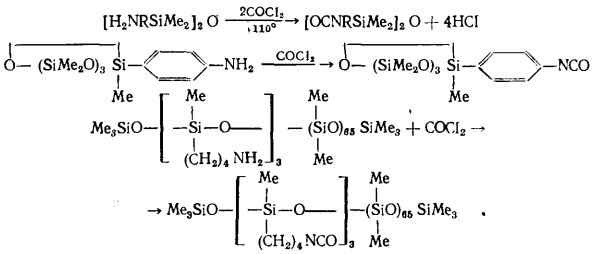
Silyl ethers of aminoalcohols of the type $R_2Si(OCH_2CH_2.NH_2)_2$ are fully cleaved by phosgene at Si–O bonds[32], but the final products have not been identified. At the same time the analogous aminophenol and aminonaphthol derivatives, both in the form of free bases and as the hydrochlorides, form the corresponding isocyanates (IX) and (X) [32,34] (see below):



(IX) (X)

$n = 1-3$; R = H, or Me.

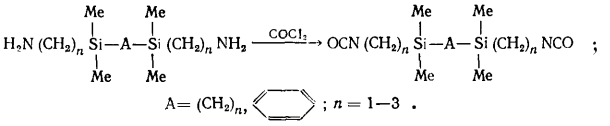
Examples of the synthesis of organosilicon mono- and di-isocyanates by treating with aminoalkylphosgene and aminophenyl derivatives of di-, tetra-, and oligo-siloxanes are known[33,35-37]:



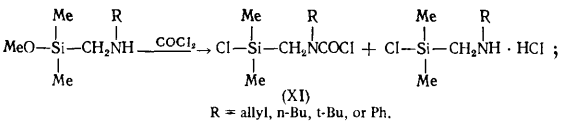
† The formation of the dimers (VIII) was also noted in the reaction of halogenoalkylsilanes with KOCN in dimethylformamide[30].

The retention of siloxane linkages on treatment with phosgene and HCl under severe conditions is doubtful, because it conflicts with the above findings, showing the undoubted cleavage of these bonds[9,14,15].

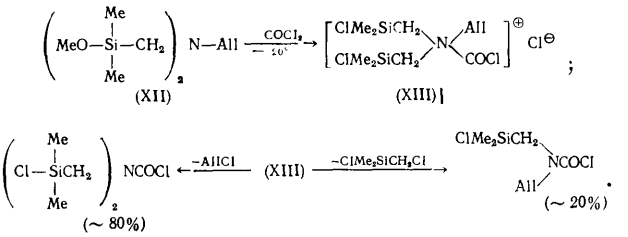
Organosilicon bifunctional monomers of another type were obtained when diamines with alkylene or phenylene bridges between silicon atoms were treated with phosgene[9,28]:



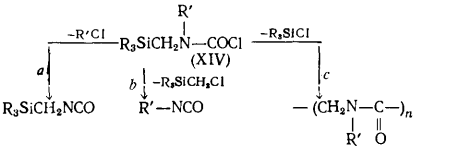
Secondary aminoalkylsilanes react with phosgene to form the corresponding organosilicon carbamoyl chlorides (XI). As for primary amines, when -Si-OAlk groups are present, they are converted into Si-Cl groups[38]:



At 20°C the tertiary organosilicon amine (XII) forms with phosgene an intermediate complex (XIII), which on heating splits off one of the substituents in the form of RCl:



It has been established that the pyrolysis of asymmetrically substituted organosilicon carbamoyl chlorides (XIV) leads to organic and organosilicon isocyanates‡. The mode of decomposition under these conditions depends on the nature of the substituents at the nitrogen and silicon atoms (see Table)[38,39]:



Silyl group	Group R′	Mode of decomposition
$ClMe_2Si$	$ClMe_2Si$	$a > c$
$ClMe_2Si$	All	$b > a + c$
Me_3Si	All	$c > a$

‡ It is known[40] that disubstituted organic carbamoyl chlorides of the type $Me_3CN(R)COCl$ (R = $PhCH_2$, allyl, or t-Bu) decompose to RNCO and Me_3CCl at 200°C.

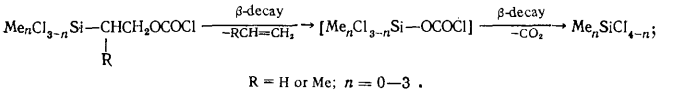
III. REACTIONS WITH COMPOUNDS HAVING SILICON-CONTAINING FUNCTIONAL GROUPS

1. COMPOUNDS CONTAINING THE SILOXANE LINKAGE

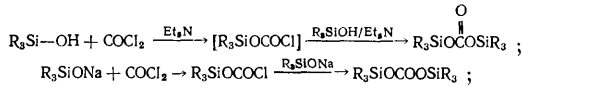
When phosgene interacts with organosilicon compounds containing the siloxane linkage (Si-O), the latter is frequently cleaved, not so much directly by phosgene as by reaction products such as HCl, carbamoyl chlorides, etc. The particular mode of the reaction involving the cleavage of the siloxane linkage is determined mainly by the nature of the atom or group X at the siloxane linkage Si-O-X.

(a) Silanols

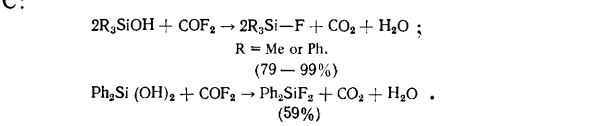
The silyl esters of chlorocarbonic acid—organosilyl chlorocarbonates (organosilyl chloroformates)—of the type $R_3SiOCOCl$, which should be formed from silanols and phosgene, are at present unknown. Such compounds are only mentioned as possible unstable intermediates[9,41,42]:



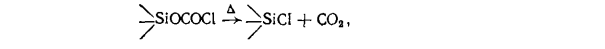
They are probably formed also in the synthesis of disilyl carbonates[16,17]:

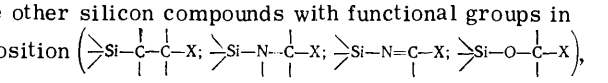


In the absence of an HF acceptor, difluorophosgene acts on silanols and silanediols as a fluorinating agent at 0°-20°C:[27]



The instability of the silyl esters of chlorocarbonic acids can be explained by their extremely high tendency towards β-elimination:



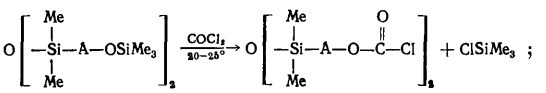
i.e. like other silicon compounds with functional groups in the β-position (), compounds of this class exhibit a distinct 1 - 4 interaction between the silicon and halogen atom (σ,σ-conjugation[43-47]). The rate of β-decomposition increases with increasing electronegativity of the group X: Cl ≫ OR > $OSiR_3$ > NR_2.[48-52]

(b) The Silyl Ethers Derived from Alcohols, Glycols, and Phenols and Silylcarboxylate Esters

Treatment of silyl ethers derived from alcohols and phenols with phosgene is in many cases preparatively preferable to the direct reaction of $COCl_2$ with the corresponding alcohols, diols, phenols, and dihydric phenols.

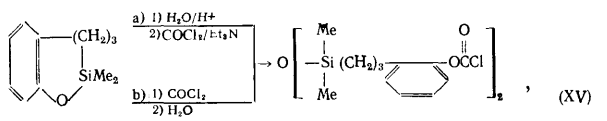
Firstly, at the end of the reaction, the reaction mixture does not contain the corrosive HCl; instead the product is chlorotriphenylsilane, which is readily

removed and which does not cleave the Si–Ar, C–O–C, Si–O–Si, and Si–O–C linkages[15–17,22,23,25,53–56], for example:



$A = CH_2$, $CH_2OCH_2CH_2$, or $CH_2CH_2CH_2$.

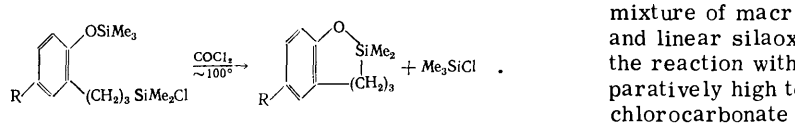
Secondly, the formation of both carbonates and chloroalkylsilanes under the influence of tertiary amines, usually employed as HCl acceptors, is fully ruled out. For example, of the following two mechanisms of the synthesis of compound (XV) (pathways *a* and *b*)



(XV)

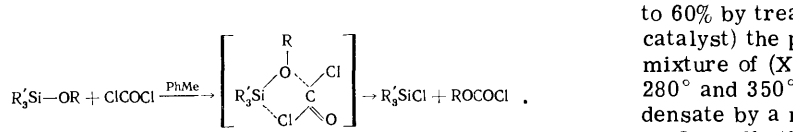
the latter is preferable, since it rules out contact between the chlorocarbonate formed and Et_3N.

Sometimes an attempt to treat substituted silylated phenols with phosgene does not lead to the required chloroformate, because the *trans*-silylation reaction is faster than the insertion of the $COCl_2$ in the Si–O bond, and the resulting heterocycles react with phosgene at much higher temperatures[16]:



As was to be expected, the reactivities of alkoxysilanes and acyloxysilanes in the reaction with $COCl_2$ proved to be different and were found to be determined by the nature of the groups incorporated in the organic and organosilicon parts of the molecule[16,55].

Reactions involving the nucleophilic substitution of the group RO in the silanes R'_3SiOR in a non-polar solvent evidently proceed via a mechanism with formation of a four-membered transition complex[40]:



Difluorophosgene reacts with alkoxysilanes like phosgene[27]. In the presence of a deficiency of COF_2 the yield of EtOCOF in the reaction with $Me_2Si(OEt)_2$ falls to 56%, since part of it is consumed in the formation of diethyl carbonate:

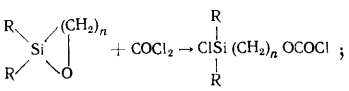
$$Me_2Si(OEt)_2 + 2EtOCOF \rightarrow Me_2SiF_2 + (EtO)_2CO .$$

Difluorophosgene does not cleave the siloxane linkage in $PhOSiMe_3$ and hexamethyldisiloxane at 20°C.

Compared with $COCl_2$ and ROCOF, aliphatic and aromatic chlorocarbonates are less reactive in relation to silyl ethers derived from alcohols and phenols. The reaction proceeds at an appreciable rate only at 120–220°C even with alkoxytrimethylsilanes which are most readily cleaved by phosgene[16,17,55,56]. As in the case of $COCl_2$, the Si–OCAr bond proved to be less reactive than Si–OCAlk.

(c) Silaoxacycloalkanes and Their Polymerisation Products

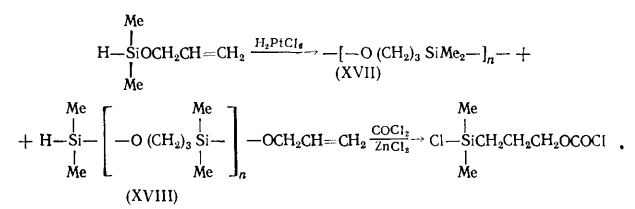
Silaoxacycloalkanes, which are cyclic silyl ethers derived from alcohols, react with phosgene, undergoing ring cleavage at the Si–O bond and giving rise to chloroformates[9,16,17,22,25,53–58]:



(XVI) R = Alk or AlkO; $n \geqslant 3$.

The reactivity falls in the series of silaoxacycloalkanes with increasing ring size[9,16,54,55]. For example, whereas silaoxacyclopentanes (XVI, $n = 3$) interact vigorously with $COCl_2$ even in the cold, the reaction of silaoxacyclohexanes (XVI, $n = 4$) with phosgene is slow even at a higher temperature (20–50°C). The reaction is sharply accelerated with increase of temperature to 100–150°C and is catalysed by Lewis acids ($ZnCl_2$, $AlCl_3$, etc.). In view of the relatively ready availability of silaoxacycloalkanes, the above reaction constitutes one of the most convenient methods for the synthesis of organosilicon monochlorocarbonates, whose yield reaches 80%.

The products of the polymerisation of silaoxacycloalkanes as well as macrocyclic silaoxacycloalkanes proved to be more passive in relation to $COCl_2$.[9,16,22,25] In particular, the study of the oligomeric product having the general formula $-[-O(CH_2)_3SiMe_2-]_n-$ and consisting of a mixture of macrocyclic silaoxa-alkanes (XVII, $n = 7–9$) and linear silaoxa-alkanes (XVIII, $n = 7–9$), showed that the reaction with phosgene does not occur even at comparatively high temperatures and the corresponding chlorocarbonate can be obtained in a yield of ~17% only in the presence of catalytic amounts of $ZnCl_2$:[9,22,54]

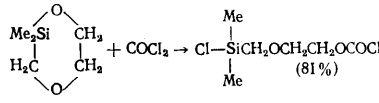


(XVII) (XVIII)

Incidentally, the yield of chlorocarbonate can be raised to 60% by treating with phosgene (in the absence of a catalyst) the products of the thermal depolymerisation of a mixture of (XVII) and (XVIII), obtain by distillation at 280° and 350°C with subsequent rapid cooling of the condensate by a mixture of dry ice and acetone[9,22,54].

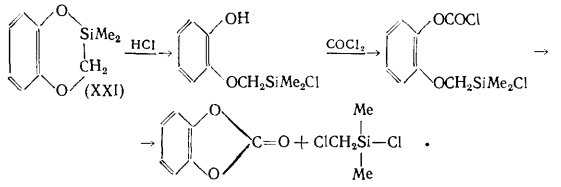
Overall, the reactivity of silaoxacycloalkanes and their condensation (dimerisation, trimerisation, etc.) products with respect to $COCl_2$ is found to be inversely related to their resistance to polymerisation.

Apart from ring strain in silacycloalkanes, the rate at which their rings are opened by phosgene is influenced also by other factors. For example, the siladioxan (XIX) reacts vigorously with $COCl_2$ and gives high yields of the chlorocarbonate (XX):[16]

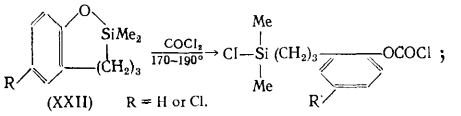


(XIX) (XX) (81%)

120–140°C and the ring is open and undergoes a rearrangement only when $COCl_2$ and gaseous HCl are passed jointly through heated (XXI):[16,24]



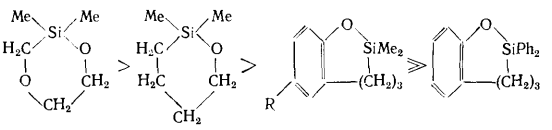
The cleavage of the Si–OC_{Ar} bond in other benzosilaoxacycloalkanes by phosgene also takes place under severe conditions at 170–190°C,[16,54] for example:



(XXII) R = H or Cl.

The replacement of methyl groups in the heterocycle (XXII) by phenyl groups makes the molecule completely inert to the action of HCl/$COCl_2$ mixture even when it remains in contact with the reagents at 200°C.

The decrease of the reactivity of silaoxacycloalkanes in the series of compounds



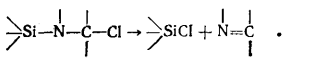
like that in the series of linear silyl ethers, is caused by the weakening of the nucleophilic properties of the O atom in the siloxane bond.

A number of procedures have been proposed for the activation of the reaction of phosgene with compounds containing the Si–O–C_{Ar} linkage. One can use Lewis acids as reaction catalysts[9,16,54], which, however, have also a side effect—the initiated decomposition of the required chlorocarbonates to alkyl(aryl) halides. Another group of initiators was therefore put forward[9,16–53]—inorganic acids or hydroxylated organic compounds. The possibility of initiating the reaction by tertiary amines (pyridine, dimethylaniline, etc.), which are capable of ionising the $COCl_2$ molecule, merits attention.

Thus the reaction of $COCl_2$ with silyl ethers—intermediates in the synthesis of glycols and dihydric phenols of the siloxane series—is of preparative value in relation to alcohol derivatives, but is of limited importance in the case of compounds with an Si–O–C_{Ar} linkage.

2. COMPOUNDS CONTAINING THE Si–N BOND

When the N–H bond in a wide variety of nitrogen-containing compounds is replaced by the N–Si bond their reaction with phosgene frequently follows another pathway. This can sometimes be accounted for by the absence of side and reversible reactions ($ClSiMe_3$ is formed instead of HCl), but the main explanation involves the formation of extremely unstable intermediates containing the σ,σ-conjugated bond system and responsible for the occurence of the irreversible β-elimination reaction



(a) Silazanes, Silylhydrazines, Cyanosilanes, and Isocyanatosilanes

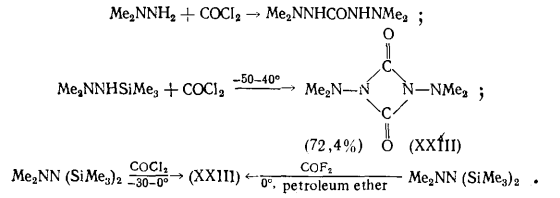
When $COCl_2$ interacts with hexamethyldisilazane, a complex mixture of products is formed[59–61]:

$$4\,(Me_3Si)_2NH + 3COCl_2 \rightarrow 5Me_3SiCl + 3Me_3SiNCO + NH_4Cl\ .$$

Sodium bis(trimethylsilyl) amide reacts with $COCl_2$ to give a 60% of *N,N'*-bis(trimethylsilyl)carbodi-imide[60,61]:

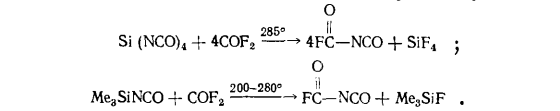
$$2\,(Me_3Si)_2NNa + COCl_2 \rightarrow Me_3SiN{=}C{=}NSiMe_3 + (Me_3Si)_2O + 2NaCl\ .$$

By protecting Me_2NNH_2 with a silyl group before its reaction with COF_2 and $COCl_2$, it was possible to obtain the dimethylaminoisocyanate dimer[62,63] instead of the corresponding urea[64], formed from dimethylhydrazine itself§:

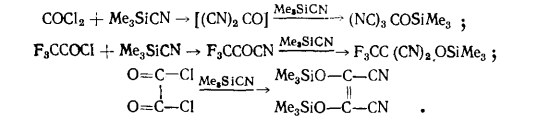


The yield of uretidinedione (XXIII) from $Me_2NN(SiMe_3)_2$ and $COCl_2$ is nearly quantitative (96.5%)[63], whereas in the reaction with COF_2 it is smaller approximately by a factor of two (46.0%)[62].

When isocyanatosilanes—$Si(NCO)_4$ or Me_3SiNCO—interact with COF_2 in an autoclave, the NCO group is substituted with formation of fluorocarbonyl isocyanates[65]:



Like trifluoroacetyl chloride and oxalyl chloride, phosgene interacts with Me_3SiCN to form the corresponding cyano-derivatives of carbonyl compounds[66]. However, dicyanocarbonyl is extremely reactive, combining with a Me_3SiCN molecule via the carbonyl group under the reaction conditions:



On treatment with Me_3SiCN, chloroformates give rise to cyanoformates[67]:

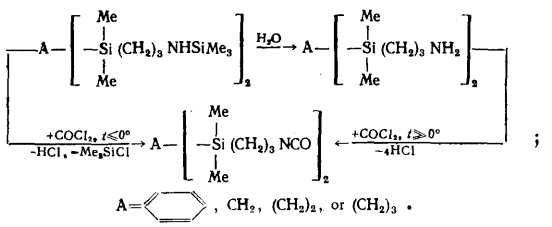
$$ROCOCl + Me_3SiCN \rightarrow ROCOCN + Me_3SiCl\ .$$

(b) *N*-Silyl-Substituted Amines

It was observed in 1969 that organosilicon di-isocyanates[9,28] are formed in high yields and under milder conditions when $COCl_2$ is allowed to react with *N*-silyl

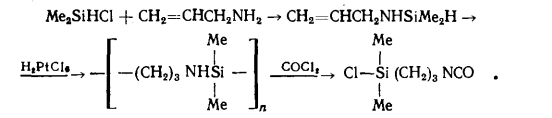
§The uretidinedione structure has been tentatively attributed[42] to the dimethylaminoisocyanate dimer (on the basis of the analysis of the infrared and ^1H NMR spectra).

derivatives of the initial amines rather than the initial amines themselves[9,68]:



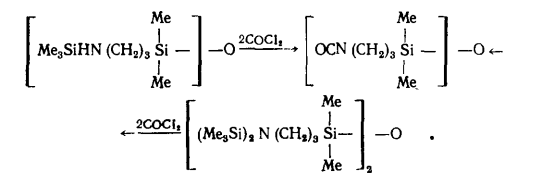
Monoisocyanates were obtained similarly[9,68-77]:

These observations made possible an exceptionally convenient procedure for the synthesis of one of the promising organosilicon monomers—γ-(chlorodimethylsilyl)propyl isocyanate—via the following mechanism[9,69,78]:

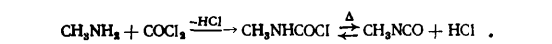


This compound had been obtained earlier as a side product in the reaction of $O-[-SiMe_2(CH_2)_3NH_2]_2$ with $COCl_2$.[9,13,14]

Subsequently it was established[9,68,69,78-83] that the reaction of phosgene with *N*-silyl-substituted primary amines is of a general type and can be used to synthesise not only organosilicon but also any other isocyanates containing groups sensitive to heat and the action of HCl, $COCl_2$, and $-NHC(O)Cl$. In particular, this made it possible to simplify the synthesis of di-isocyanates of the disiloxane series which has been difficult to obtain previously[9,69]:

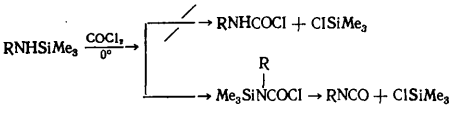


A detailed study of this new reaction in relation to many examples[9,68-84] showed that, on treatment with phosgene, any primary *N*-silyl-substituted amines give rise to high yields of the corresponding isocyanates at appreciably lower temperatures (between −60° and 0°C) than the initial free amines. The latter factor revealed particularly clearly the advantages of the above method for the synthesis of lower isocyanates[69-77]. For example, it is known that treatment of methylamine with phosgene results in the formation of methylcarbamoyl chloride, which begins to decompose at temperatures of 100°C to methyl isocyanate and hydrogen chloride:



However, the latter reaction is reversible and the separation of gaseous methyl isocyanate and hydrogen chloride is extremely difficult. The dehydrochlorination of methylcarbamoyl chloride is therefore usually carried out with the aid of organic or inorganic bases. This applies equally to the synthesis by a similar procedure of ethyl, allyl, and other low-boiling isocyanates.

On the other hand, the reaction of *N*-silyl-substituted amines with phosgene, which leads to the formation of the extremely unstable *N*-silylcarbamoyl chloride[9,68,69,79,80], decomposing irreversibly to an alkyl isocyanate and chlorotrimethylsilanes, can serve as a new and convenient preparative method for the synthesis of lower alkyl isocyanates[9,68-83]:



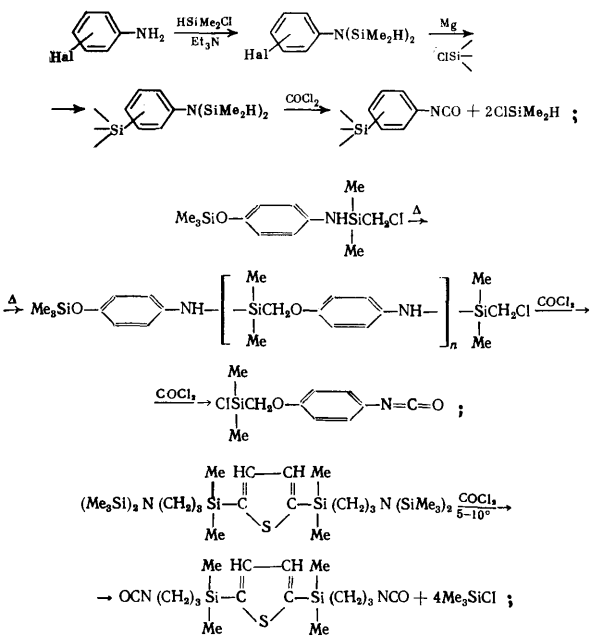
The occurrence of the reaction via the upper pathway is ruled out, since it is known that alkylcarbamoyl chlorides are stable up to ~100°C, while the above reaction takes place almost quantitatively at temperatures below zero.

On the other hand, the probability of ready dehydrochlorination of alkylcarbamoyl chlorides under the reaction conditions (under the influence of aminosilanes or the chlorosilanes formed) is low, and special experiments showed that, for example, methylcarbamoyl chloride does not change even after prolonged refluxing with chlorosilanes[9,69].

Nevertheless, the Si–N bond is also very readily cleaved by phosgene. For example, the reaction with *N*,*N*-disilyl-substituted amines takes place at low temperatures and the yield of the corresponding isocyanates is sometimes actually better, owing to the complete absence of hydrogen chloride, than in the reaction employing *N*-monosilyl-substituted amines[9,12,69-86]:



It must be emphasised that, when silyl-substituted amines are treated with phosgene, the corresponding silyl chloride, used to introduce a protective silyl group into the initial amines, is almost quantitatively regenerated. The above findings give rise to the hope that certain isocyanates (for example, methyl isocyanate) will be synthesised not only in the laboratory but also under industrial conditions[15]. Simple methods for the synthesis of certain organosilicon, organotin, and organogermanium isocyanates, which are of preparative value but are difficult to obtain, are presented below[9,15,78,81,82,85-89]:



$$Bu_3Sn(CH_2)_3NHSiMe_3 \xrightarrow{COCl_2} Bu_3Sn(CH_2)_3NCO\ ;$$

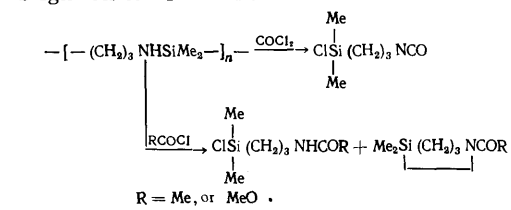
$$Bu_3Sn(CH_2)_3N(SiMe_3)_2 \xrightarrow{COCl_2} Bu_3Sn(CH_2)_3NCO\ ;$$

$$Et_3Ge(CH_2)_3NHSiMe_3 \xrightarrow{COCl_2} Et_3Ge(CH_2)_3NCO\ .$$

N-Silyl-substituted secondary amines undergo an exothermic reaction with phosgene, giving an almost quantitative yield of a trialkylchlorosilane and the corresponding dialkylcarbamoyl chloride[9]:

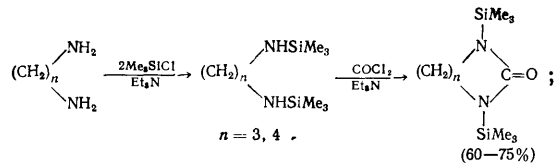
$$R_2N{-}SiMe_3 + COCl_2 \xrightarrow[-15-0^\circ]{} \underset{(88\%)}{R_2NCOCl} + \underset{(97\%)}{Me_3SiCl}\ .$$

It is appropriate to mention here that the Si–N bond in aminosilanes is cleaved by acyl halides and chlorocarbonates at a much lower rate than in the case of $COCl_2$.[38, 59, 90–92] This follows, for example, from the fact that in the absence of a catalyst (concentrated H_2SO_4), the compounds ROCOCl do not interact with $R'N(SiMe_3)_2$ even on heating[38, 91]. Slow acylation of the oligomer $-[-(CH_2)_3NH.SiMe_2-]_n$ with methyl chlorocarbonate or acetyl chloride is accompanied by the competing dehydrochlorination reaction, which on treatment with phosgene takes place to only a slight extent if at all:



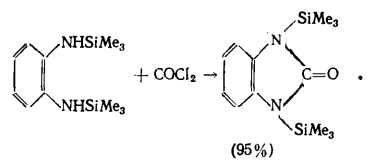
R = Me, or MeO .

A departure from the general rule governing the interaction of phosgene is shown by certain silylated diamines[93]:



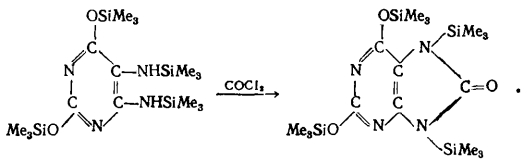
$n = 3, 4$.

Under the same conditions, *N*,*N*′-bis(trimethylsilyl)-*O*-phenylenediamine reacts with $COCl_2$ to form *N*,*N*′-bis-(trimethylsilyl)-2-benzimidazolone in a high yield[93]:

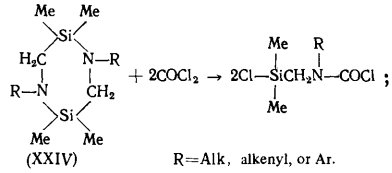


(95%)

2,4-Bis-(*O*-trimethylsilyl)-5,6-bis(trimethylsilylamino)-uracil, formed on silylation of 5,6-diaminouracil, reacts with $COCl_2$ in toluene to form tetrakistrimethylsilyluric acid[93]. Without the protection of the *N*-functional group by silylation, this reaction does not occur. The above synthesis is remarkable also because, by virtue of silylation, the reaction with 5,6-diaminouracil can be carried out in a hydrocarbon solvent[93]:

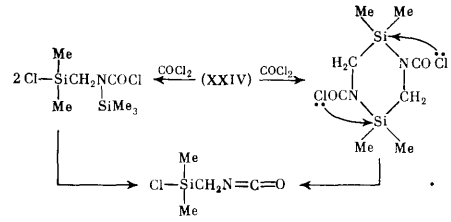


The ease of the cleavage of the 2,5-disilapiperazine ring in compound (XXIV) by phosgene combined with the complete absence of any side products makes this reaction extremely promising for preparative purposes[38]:

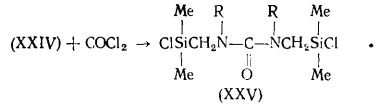


(XXIV) R=Alk, alkenyl, or Ar.

When R = $SiMe_3$, the reaction does not stop at the stage involving the formation of carbamoyl chloride, since its β-decomposition causes its dechlorosilylation to the isocyanate:

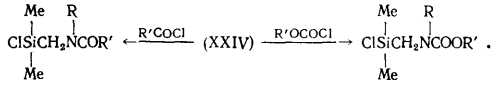


It has been shown[38] that, whereas the isocyanate is formed regardless of the order in which the reactants are mixed when R = $SiMe_3$, in the remaining cases a constant excess of $COCl_2$ must be ensured in the course of the reaction in order to obtain carbamoyl chlorides. Otherwise the ureas (XXV) are produced:



(XXV)

The disilapiperazine ring is readily cleaved by chlorocarbonates and carboxylic acid chlorides with formation of urethanes and amides respectively[38]:



(d) Silyl Derivatives of Aminoacids

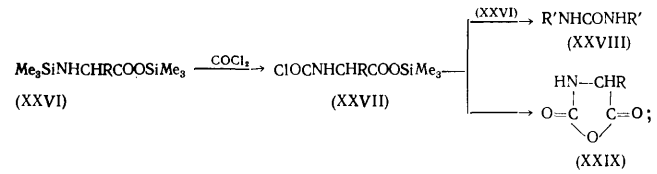
The reaction of phosgene (thiophosgene) with silyl derivatives of aminoacids is used particularly frequently in the synthesis of esters of isocyanatocarboxylic acids and *N*-carboxyanhydrides.

The interest in the esters of isocyanatocarboxylic acids is due primarily to the fact that, in combination with *N*-protected aminoacids, they can be regarded as convenient intermediates in the stepwise synthesis of di- and poly-peptides.

The silyl esters of isocyanatocarboxylic acids are much more readily hydrolysed than alkyl esters and some workers[94] have for this reason regarded them also as a potential source of free isocyanatocarboxylic acids O=C=NCH(R)COOH which had been little studied hitherto and which have been frequently mentioned in the literature as possible highly reactive monomers for the synthesis of polypeptides and polyamides (the intermediate formation of these compounds was postulated, particularly, in a study of the polymerisation of *N*-carboxyanhydrides).

N-Carboxyanhydrides of aminoacids (also referred to as oxazolidine-2,5-diones or leuchs anhydrides) are in their turn convenient and frequently employed starting compounds for the synthesis of polyaminoacids.

Thus Kricheldorf[95] showed that the trimethylsilyl esters of *N*-trimethylsilylaminoacids (XXVI) react with phosgene, eliminating Me_3SiCl and forming initially the silyl esters of *N*-chloroformylaminoacids (XXVII), which then either react with the initial substance to give urea derivatives (XXVIII) or cyclise to oxazolidine-2,5-diones (XXIX):



(XXVI) (XXVII) (XXVIII) (XXIX)

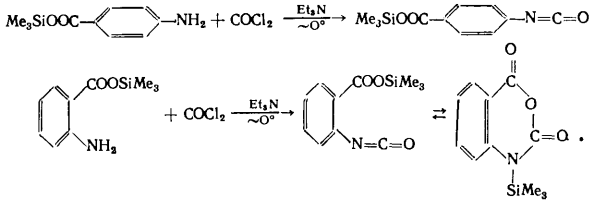
R′=CHRCOOSiMe$_3$.

The formation of the urea derivative in this reaction can be avoided by using an excess of phosgene and by adding slowly the silylated aminoacids to the latter[95]. Intramolecular cyclisation is favoured by an increased temperature and a branched structure of the hydrocarbon residue of the aminoacid.

The advantage of this method of synthesising *N*-carboxyanhydrides of aminoacids over known methods is that it does not entail the evolution of hydrogen chloride, which permits a retention of the ester groups and of the multiple bonds in the molecule. In particular, the *N*-carboxyanhydride of *O*-trimethylsilyl-L-tyrosine was obtained by this procedure in a satisfactory yield[95]. For comparison, one may note that the formation of this product by silylating the *N*-carboxyanhydride of L-tyrosine with the Me_3SiCl/Et_3N mixture cannot be achieved, because the product of this reaction polymerises after a short time.

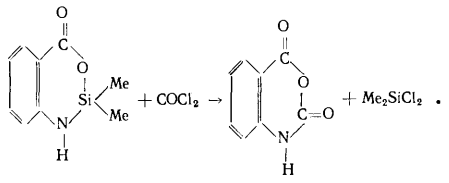
The use of silyl esters (in contrast to the *N*-benzyloxycarbonylaminoacids normally employed) also has the advantage that most of them can be vacuum distilled without decomposition[96]. Thus silylation (and subsequent distillation) can serve as a convenient method for purifying the initial aminoacids or their derivatives, which frequently show only a small capacity for crystallisation. Furthermore, in contrast to aminoacids with a free carboxy-group, silyl esters dissolve even in non-polar solvents (for example, in petroleum ether), which makes it possible to eliminate the initial substance as an impurity in the *N*-carboxyanhydride, which is precipitated[96].

Mono- and *N*, *O*-bis-silyl derivatives of aromatic aminoacids react with phosgene to form different products, depending on the conditions. Whereas in the absence of Et_3N monosilyl derivatives form mainly polymeric compounds (or the anhydride of isatinic acid in the case of the *O*-trimethylsilyl ester of anthranilic acid), the reaction in the presence of Et_3N makes it possible to obtain high yields of trimethylsilyl esters of isocyanatocarboxylic acids whose *ortho*-derivatives show a tendency towards tautomeric transformations[87]:



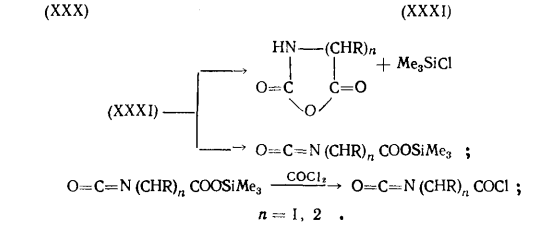
N,*O*-Bis-silyl derivatives can react with $COCl_2$ under mild conditions (0–20°C) to form trimethylsilyl esters of isocyanatocarboxylic acids also in the absence of Et_3N, whereas under more severe conditions polymeric products having tentatively the uretidine dione structure are formed[87].

The action of phosgene on 4,4-dimethyl-1,6-benzo-3-oxa-4-sila-5-aza-2-cyclohexanone leads to the virtually quantitative formation of the anhydrides of isatinic acid:



N,*O*-Bis-silylated *N*-acylaminoacids react with phosgene with difficulty at 80°C; *N*-carboxyanhydrides are formed in this case with a low yield[95]. The reactions described proceed without the inversion of configuration[95].

Above 0°C, the trimethylsilyl esters of *N*-siloxycarbonylaminoacids (XXX) react readily with phosgene, eliminating two Me_3SiCl molecules and forming *N*-carboxyanhydrides[97]. The *N*-siloxycarbonyl group then exhibits a higher reactivity than the *C*-siloxycarbonyl group, as a result of which trimethylsilyl esters of *N*-halogenocarbonylaminoacids (XXXI) are formed as intermediates, which then cyclise to form *N*-carboxyanhydrides[97,98]. The esters of halides of isocyanatocarboxylic acids are formed as side products, which predominate in the case of β-aminoacids[97]:

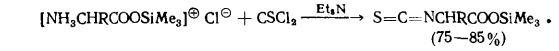


(XXX) (XXXI)

n = 1, 2 .

Since alkoxy- and aryloxy-trimethylsilyl groups are still less reactive than trimethylsiloxycarbonyl groups (the reactivity of various siloxy-groups in relation to acid chlorides diminishes in the sequence $R_2NCOOSiMe_3 > RCOOSiMe_3 > AlkOSiMe_3 > ArOSiMe_3$), [96] the reaction with phosgene by this procedure can yield *N*-carboxyanhydrides containing silyl substituted alcoholic or phenolic groups[97,98]. The above method for the synthesis of *N*-carboxyanhydrides have also the advantage that, compared with the established procedure, it makes it possible to obtain them in higher yields (>90%) and with a very high degree of purity. It is also superior to the synthesis of *N*-carboxyanhydrides from trimethylsilylesters of *N*-trimethylsilylaminoacids discussed above, since in this case the risk of the formation of urea by a side reaction is eliminated.

The interaction of thiophosgene with the hydrochlorides of the trimethylsilyl esters of aminoacids is one of the most convenient preparative methods for the synthesis of trimethylsilyl esters of isothiocyanatocarboxylic acids according to Kricheldorf's data[99]:



(75–85%)

These acids can be used[100] as convenient intermediates in the synthesis of free isothiocyanatocarboxylic acids¶ (S=C=NCHRCOOH) and thiazolidine-2,5-diones.

On passing from trimethylsilyl esters to ordinary esters of aminoacids silylated at the nitrogen atom, the interaction with $COCl_2$ terminates with the formation of the corresponding derivatives of isocyanatocarboxylic acids[101]:

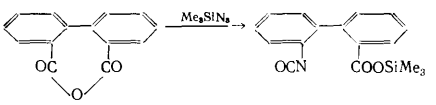
$$Me_3SiNHCHRCOOEt \xrightarrow[0^\circ]{COCl_2} OCNCHRCOOEt\ ;$$

R=Me, or iso-Pr.

The possibility of using PhOCOCl instead of $COCl_2$ for the synthesis of these compounds has been demonstrated:

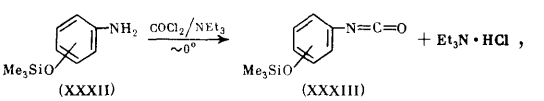
$$NH_2(CH_2)_4COOH \xrightarrow[3)\ Et_3N]{1)\ Me_3SiCl;\ 2)\ PhOCOCl} OCN(CH_2)_4COOSiMe_3 + PhOSiMe_3$$

or one can use a phosgene-free method[102]:



(e) Silyl Derivatives of Aminophenols

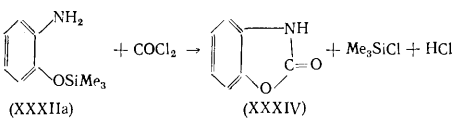
Silyl derivatives of aminophenols react vigorously with phosgene to form a wide variety of products. Thus, whereas siloxyanilines (XXXII) are converted into the corresponding isocyanates (XXXIII, a and b) on treatment with phosgene under mild conditions (~0°C) and in the presence of Et_3N, [88]



(XXXII) (XXXIII)

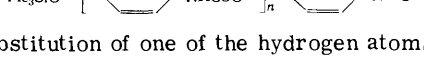
[*a*) *ortho*-isomer; *b*) *para*-isomer]

when the temperature is raised in steps (initially 20–40° and then 100–110°C), isocyanates are not formed, since the Si–OC bonds are ruptured. The main product in the reaction of (XXXIIa) is the benzoxazolinone (XXXIV)[88]:

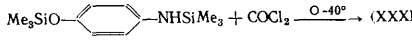


(XXXIIa) (XXXIV)

while the reaction of (XXXIIb) gives rise to an oligomer:

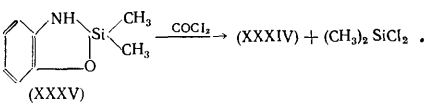


The substitution of one of the hydrogen atoms in the NH_2 group by the trimethylsilyl residue makes it possible to obtain the isocyanate (XXXIIIb) from the para-isomer[88]:



However, the yield of the product is low, since even under the mild conditions employed the reaction is accompanied by the formation of a polymer having the above structure via a side process.

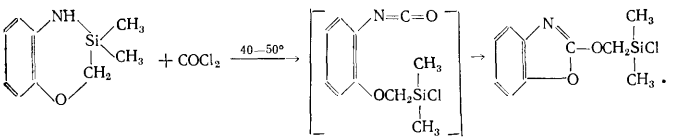
The Si–OC bond is even more readily cleaved in the cyclic compound (XXXV), whose reaction with $COCl_2$ results in its complete conversion into benzoxazolinone even at a temperature of –40°C and below:



(XXXV)

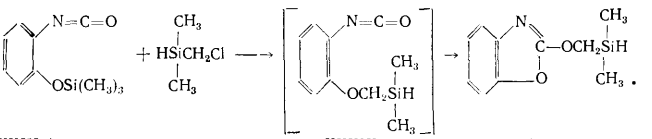
This increase of reactivity can be accounted for by the increased polarisation of the Si–O bond owing to the reduced amount of double bond character of the linkage between the O and Si atom due to the inclusion in the silicon *d* orbital of the free electron pair not only at the oxygen atom but also at the nitrogen atom.

The reaction of $COCl_2$ with the cyclic compound (XXXVI) had an unexpected course: instead of the expected isocyanate, a high yield was obtained of the isomeric product (XXXVIII). Evidently, the isocyanate (XXXVII) formed in the first stage is unstable and isomerises rapidly to (XXXVIII):



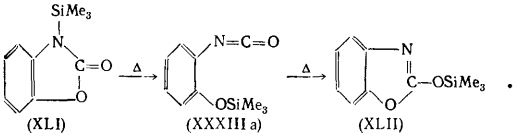
(XXXVI) (XXXVII) (XXXVIII)

The instability of isocyanates containing silylmethoxy-groups as well as Me_3SiO groups in the *ortho*-position relative to NCO was confirmed also by studies on a number of other reactions[88]. Thus the transalkylation of *o*-trimethylsiloxyphenyl isocyanate (XXXIIIa) by reaction with chloromethyldimethylsilane results in the evolution of up to 85% of the theoretical amount of Me_3SiCl, but instead of the isocyanate (XXXIX) the product is the isomeric compound (XL):



(XXXIII a) (XXXIX) (XL)

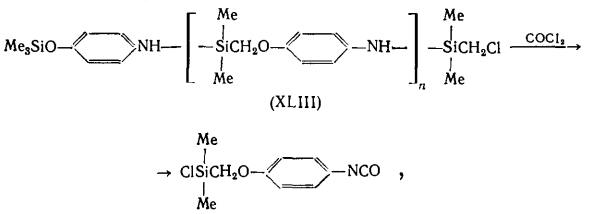
The initial product of this reaction—*o*-trimethylsiloxyphenyl isocyanate (XXXIIIa)—is the most stable of the *o*-substituted phenyl isocyanates examined. It can be isolated in an analytically pure form by vacuum distillation and is stable on storage. Nevertheless, under comparatively severe conditions this compound is capable of cyclising. For example, it has been observed that *N*-trimethylsilylbenzoxalinone (XLI), formed when benzoxalinone is treated with chlorotrimethylsilane in the presence of Et_3N, undergoes intramolecular β-elimination even under the conditions of its formation (80°C) and is converted into *o*-trimethylsiloxyphenyl isocyanate (XXXIIIa). On heating (3 h, 160–200°C), the latter isomerises to the benzoxazolinone derivative (XLII)[43,88]:



(XLI) (XXXIII a) (XLII)

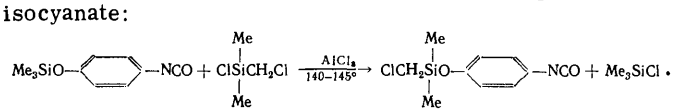
¶ β-, γ-, and ε-isothiocyanatocarboxylic acids and their silyl esters are exceptionally active physiologically, giving rise to a very severe rash. Even in very low doses, they can cause painful blisters and wounds[100].

In contrast to *o*-derivatives, *p*-siloxyphenyl isocyanates are quite stable can be obtained not only via the reactions discussed above but also on treatment of the polymer (XLIII) with phosgene[88]:



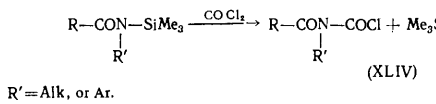
(XLIII)

and by the transalkylation of *p*-trimethylsiloxyphenyl isocyanate:



(f) *N*-Silyl-Substituted Carboxylic Acid Amides

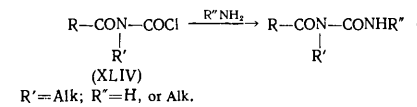
N-Acylcarbamoyl chlorides. The reaction of *N*-alkyl(aryl)-*N*-(trimethylsilyl)-amides with phosgene was found to give high yields of the first examples of a hitherto unknown class of organic compounds—*N*-alkyl-(aryl)acylcarbamoyl chlorides (XLIV)[9,43,80,84,103,104]:



(XLIV)

R′=Alk, or Ar.

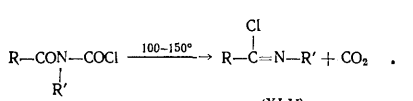
It has been shown[9,43,104] that *N*-acyl-*N*-alkylcarbamoyl chlorides (XLIV) are converted into *N*-acyl-*N*-alkylureas on treatment with aqueous ammonia:



(XLIV)

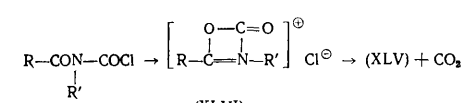
R′=Alk; R″=H, or Alk.

When acylcarbamoyl chlorides (XLIV) are heated to 100–150°C, they undergo quantitative decarboxylation to the corresponding imidochlorides (XLV)[9,43,80,84,103,104]:



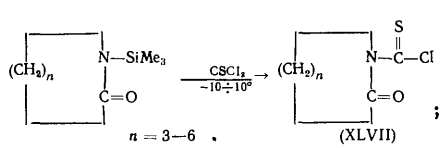
(XLV)

Presumably the decomposition of these compounds proceeds via the intermediate formation of the salt (XLVI)[43,104]:



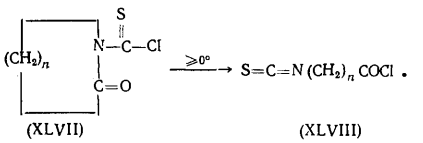
(XLVI)

Lactams silylated at the nitrogen atom, which are cyclic amides, interact with thiophosgene via a similar mechanism[105]:



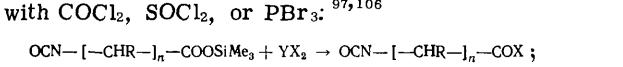
$n = 3-6$. (XLVII)

However, *N*-chlorothioformyl derivatives (XLVII) isomerise even at 0°C to the chlorides of ω-isothiocyanatocarboxylic acids (XLVIII), which can be isolated in a pure form:



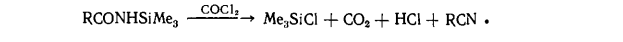
(XLVII) (XLVIII)

The oxygen analogues of the acid chlorides (XLVIII), i.e. the chlorides of isocyanatocarboxylic acids, have been obtained by treating the silyl esters of isocyanatocarboxylic acids with $COCl_2$, $SOCl_2$, or PBr_3:[97,106]

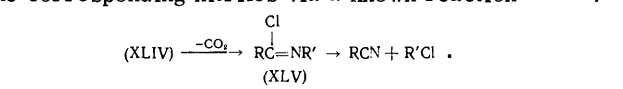


R = H or Alk; n = 1,2; X=Cl, or Br; Y=SO, CO, or PBr .

In contrast to *N*-alkyl(aryl)-*N*-silyl-substituted amides, *N*-silyl-substituted amides give rise to the corresponding nitriles on reaction with phosgene (at temperatures not exceeding room temperature)[9,43,84,103,104]:



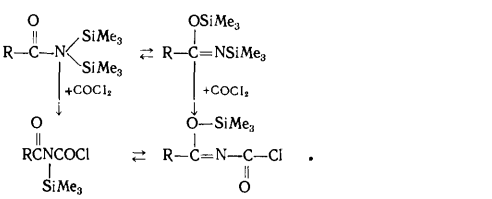
Presumably here too the reaction proceeds, as in previous instances, via the formation of acylcarbamoyl chlorides (XLIV, R′ = H), which subsequently decompose to the imidochlorides (XLV), and the latter are converted into the corresponding nitriles via a known reaction[9,103,104]:



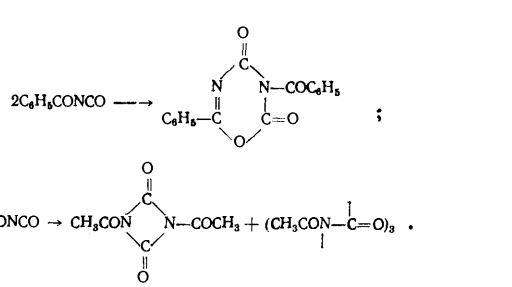
(XLV)

In contrast to compounds with R′ = alkyl or aryl, acylcarbamoyl chlorides with R′ = H apparently have extremely low thermal stabilities. Similar relations are known to be characteristic also of the imidochlorides RC(Cl)=NR′, which are also extremely unstable when R′ = H.

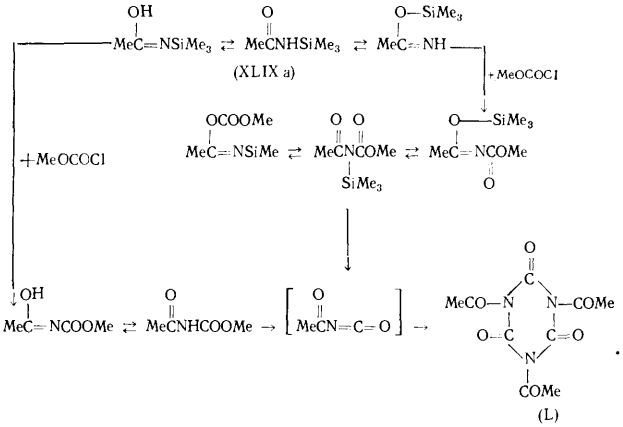
Disilyl substituted carboxylic acid amides react very vigorously with phosgene and form a mixture of di- and tri-meric forms of the acyl isocyanate[38,43,107]. The reactions probably proceed via mechanisms involving the formation of *N*-silyl substituted acylcarbamoyl chlorides with the Si–N–C–Cl system of conjugated bonds[43]:



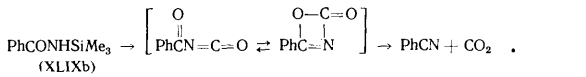
β-Decomposition of these compounds leads to acyl isocyanates, which undergo further reactions:



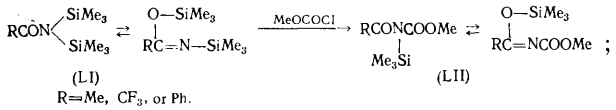
Monosilyl-substituted acetamides and benzamides react in different ways with methyl chloroformate, depending on their possible tautomeric forms: the reaction of silylated acetamide (XLIXa) led to the isolation of triacetyl isocyanurate (L) as a result of the following probably reactions:



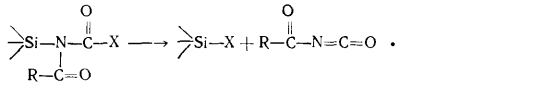
However, the monosilylbenzamide (XLIXb) is converted into benzonitrile under these conditions. The difference between the final reaction products is caused by the tendency of benzoyl isocyanate, which is stable under other conditions, to eliminate CO_2:



In the course of the study of the reaction of disilyl-substituted amides (LI) with chloroformates a new class of organo silicon compounds was obtained, namely the esters of silyl-substituted acylcarbamic acids (LII):[43]



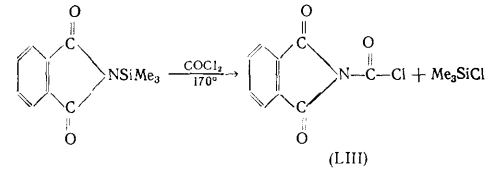
The possibility of isolating these compounds in a pure state, in contrast to the related *N*-silyl-substituted *N*-acylcarbamoyl chlorides, is due to the significantly lower electronegativity of the alkoxy- groups in the β-position relative to the silicon atom in the system of conjugated bonds $\equiv Si-\overset{|}{N}-\overset{|}{C}-X$ (X = OAlk or Cl) and the consequent lower tendency towards β-decomposition:



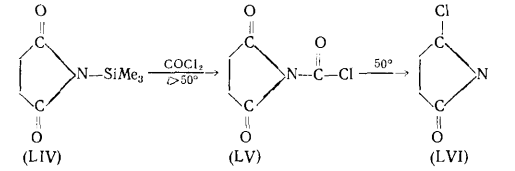
The reactivity of the amides (LI) is greatly influenced by the electronegativity of the substituent R, which is ultimately responsible, on passing from the methyl to the phenyl and trifluoromethyl groups, for the weakening of the nucleophilic properties of the molecule as a whole. Indeed, whereas bis(trimethylsilyl)acetamide (LI, R = Me) reacts readily with methyl chloroformate, the phenyl analogue (LI, R = Ph) requires the presence of catalytic amounts of H_2SO_4, as in the reaction of disilyl-substituted amines. The disilyl derivative of trifluoroacetamide does not undergo this reaction at all.

Carboxylic acid amides are known to be weaker bases than amines. Since silylation at the nitrogen atom lowers the basicity of compounds, the disilyl-substituted amides should be still weaker bases and hence should be less reactive in relation to chloroformates than the corresponding amines. The observed enhanced reactivity of disilyl derivatives of acetamide and benzamide can be accounted for by their interaction with chloroformates in the imidol form.

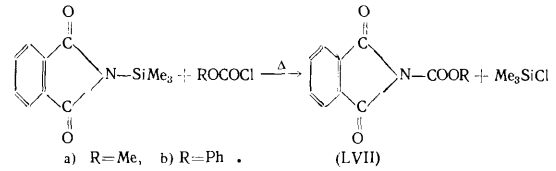
N,N-Diacylcarbamoyl chlorides[107,108]. In contrast to *N*-acyl-*N*-alkyl(aryl)carbamoyl chlorides, *N*-chlorocarbonylphthalimide (LIII), i.e. the first representative of *N,N*-diacylcarbamoyl chlorides, is formed only under very severe conditions, for example, in boiling pseudocumene on treatment of *N*-trimethylsilylphthalimide with phosgene:



On the other hand, *N*-trimethylsilylsuccinimide (LIV) reacts vigorously with $COCl_2$ and *N*-chlorocarbonylsuccinimide (LV) is decarboxylated under the reaction conditions to 2-chloro-Δ^1-5-pyrrolinone (LVI):



N-Trimethylsilylphthalimide reacts with methyl and phenyl chloroformates as well as $COCl_2$, undergoing cleavage at the Si–N bond and giving rise to the corresponding *N*-methoxycarbonyl- and *N*-phenoxycarbonylphthalimides (LVII, a and b):

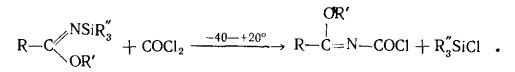


The thermal stability of the *N*-phenoxycarbonyl derivative of phthalimide is higher than that of *N*-chlorocarbonylphthalimide; it is decarboxylated only in boiling hexamethylphosphoramide (230–240°C).

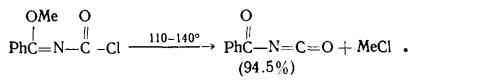
(g) *N*-Silyl-Substituted Iminoesters and Amidines

N-Silyl-substituted iminoesters proved to be much more stable than the initial iminoesters, which makes it possible to use them in reactions which had been previously difficult to control.

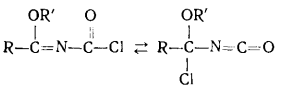
For example, it has been observed[109] that, when iminoesters are acted upon by phosgene, *N*-chlorocarbonyliminoesters are formed. The reaction of phosgene with *N*-silyliminoesters proceeds under incomparably milder conditions and leads to the formation of *N*-chlorocarbonyliminoesters in much higher yields[43,80,110]:



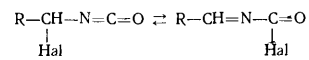
The *N*-chlorocarbonyliminoesters obtained are thermally unstable and tend to form acyl isocyanates on heating[43,80,110]:



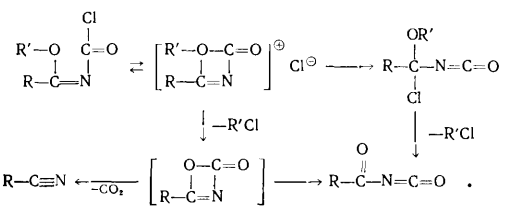
Apart from the intense absorption bands due to the C=N (1640 cm^{-1}) and C=O (1760 cm^{-1}) groups, the infrared spectra of *N*-chlorocarbonyliminoesters contain a weak absorption band due to the N=C=O group at 2252 cm^{-1}. The simultaneous presence of these bands in the spectra of compounds of this kind is explained[109] by the tautomeric equilibrium



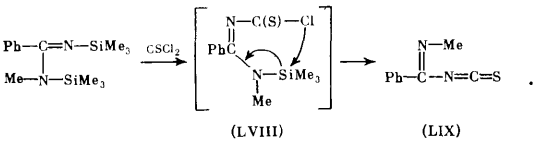
which is analogous to the familiar equilibrium of α-halogeno-substituted isocyanates[111]:



However, we believe that one cannot rule out the possibility also that *N*-chlorocarbonyliminoesters exist in the form of transitional "onium" complexes, which undergo the following reactions[43]:

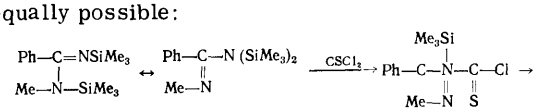


Having studied the reaction of *N*-methyl-*N*,*N*'-bis-(trimethylsilyl)benzamidine with thiophosgene, Barnikow and Ebeling[112] put forward the following mechanism for the formation of *N*-methylbenzimidoisothiocyanate (LIX):



(LVIII) (LIX)

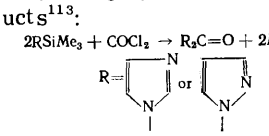
However, one should note that at least two other versions are equally possible:



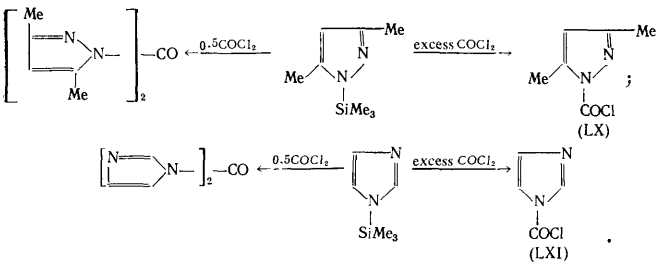
(LVIII) ↔ (LIX) .

(h) *N*-Silyl-Substituted Azoles

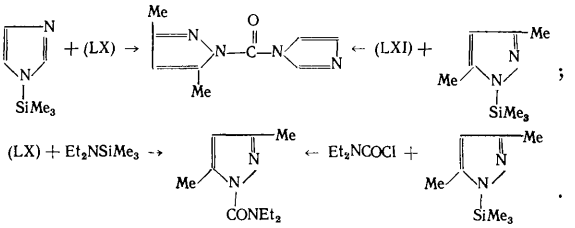
As early as 1960, Birkofer et al. showed that *N*-trimethyl-substituted diazoles react almost quantitatively with phosgene at 0–20°C to form the corresponding acylation products[113]:



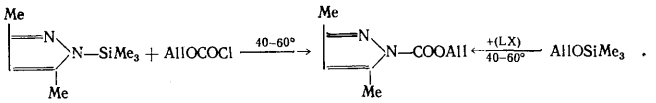
However, it was found that the nature of the final products is determined by the ratio of the initial reactants and the order in which they are introduced into the reaction:



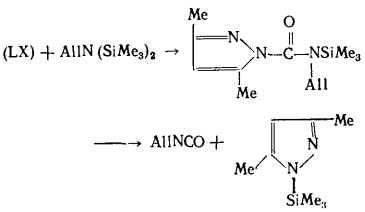
Carbamoyl chlorides (LX) and (LXI) as well as Et_2NCOCl react with *N*-silyl-substituted azoles to form symmetrically and asymetrically constructed carbonyl compounds[90]:



In contrast to $COCl_2$ and carbamoyl chlorides, allyl chlorocarbonate is less reactive in relation to *N*-trimethylsilyldiazoles and react with the latter on heating:



The carbamoyl chlorides (LX) and (LXI) react with $AllN(SiMe_3)_2$ to form the corresponding urea, whose pyrolysis under the conditions of the synthesis leads to AllNCO:



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The Etherates of Organoaluminium Compounds

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The literature data on the synthesis and chemical and physicochemical properties as well as the applications of the etherates of organoaluminium compounds are considered systematically and critically. The similarity and differences between the properties of the etherates and ether-free aluminium alkyls are demonstrated and the applications of the etherates of aluminium alkyls are discussed.
The bibliography includes 321 references.

CONTENTS

I. Introduction 487
II. The etherates of aluminium trialkyls 487
III. The etherates of alkylaluminium halides 491
IV. The etherates of organoaluminium compounds of the type R_2AlY (Y = H, OR, NR_2, etc.) 492
V. The etherates of unsaturated organoaluminium compounds 493
VI. The etherates of other organoaluminium compounds 494
VII. The reactivity of etherates 494
VIII. The applications of etherates 495

I. INTRODUCTION

The application of organoaluminium compounds (OAC) have been greatly extended recently[1-6], but many difficulties arise in studies involving OAC due to their highly corrosive nature. A number of workers have found that many chemical reactions of OAC are characteristic of their etherates, which have been more readily available and are more convenient to handle and therefore can be used successfully instead of the ether-free OAC. Furthermore, examples are known where the use of etherates involves the manifestation by the latter of completely specific properties.

No attempts have been made to survey the literature data on OAC etherates, probably because the principal results concerning the specific features of these compounds have been obtained during the last ten years and their importance is still not adequately recognised[5,6]. The available reviews of OAC coordination complexes, including individual data on etherates, are based on results published up to the beginning of the 1960s [1,7-10] or are devoted to special problems (polymerisation[11,12], ligand exchange[13,14]). A monograph[15] deals with the literature up to 1966, mainly concerning various aspects of physicochemical studies on aluminium complexes; another publication[16] is descriptive.

The aim of the present review is to draw the attention of investigators to certain aspects of the chemistry of OAC etherates and to the possibility of their employment. The review deals systematically and critically with the literature data of the synthesis, physicochemical and chemical properties, and applications of the etherates of OAC complexes published mainly during the last decade. The properties of the etherates are compared with those for the ether-free aluminium alkyls. The influence of complex formation on OAC reactions is discussed. The tables present the constants of the most typical etherates among those which have not been included in the reviews mentioned above.

The conclusions reached can be used in considering many general problems of the chemistry of organometallic compounds, including the chemistry of complexes of aluminium alkyls with S-, N-, and P-organic donors.

II. THE ETHERATES OF ALUMINIUM TRIALKYLS

1. Composition and Structure

It has been established by various methods that the composition of the etherates usually corresponds to monomeric 1:1 complexes having the general formula $R_3Al.OR_2$. This composition is most likely for monofunctional ethers and aluminium alkyls with not unduly cumbersome side groups[7,8,17-23], but in the case of t-butyl compounds stoichiometry breaks down[23-25].

Bi- and poly-functional ethers can combine with several aluminium alkyl molecules. Dioxan[20-23,26], monoglyme[27,28], diglyme[28,29] and *p*-dimethoxybenzene[30] form stable 1:2 adducts; the 1:1 compounds are labile and exist in the presence of an excess of the donor. Acetals give rise to both 1:1 and 2:1 complexes[23,31]. The formation of complexes of triethylaluminium with dimethyl[29] and diethyl[31] ethers of ethylene glycol, the dimethyl ether of tetraethylene glycol[31], and polyethers with higher molecular weights[6,32,33] involves the attainment of an Al:O ratio of 1:1. However, the products formed are unstable and on heatin *in vacuo* split off part of their aluminium trialkyl and are converted into compounds of the type

$$-O-CH_2CH_2-O-CH_2CH_2-$$
$$\downarrow$$
$$AlEt_3$$

Complex formation with a single oxygen atom in such systems (ΔH = 10–10.5 kcal mole) reduces the electron donating properties of the neighbouring oxygen atom to such an extent that the next AlR_3 molecule is coordinated via at least one heteroatom, reducing still more the basicity of the oxygen which has not reacted[31,34]; this atom is the last to be coordinated (ΔH = −1.5–4 kcal mole^{-1} [31]).

Owing to steric hindrance, substituted poly(vinyl ethers) react with iso-Bu_3Al via only some of the ether groups[23]. Even in the presence of a triple excess of the acceptor, the degree of complex formation never reaches

50%. Furthermore, steric hindrance depends on the regularity of the polymer structure. It is noteworthy that, depending on the conditions (the state of aggregation, the concentration of the solution, temperature, etc.), polymeric ligands assume different conformations and possibilities are created for the occurrence of a wide variety of modes of coordination [23,32]. Systematic study of the formation of complexes by AlR_3 with polydentate ligands will assist in providing an answer to a number of questions concerning the specific features of the behaviour of such complexes in certain reactions (see, for example, Ivanov et al. [35]).

On the basis of spectroscopic data [17,18,36], the structure with C_S symmetry (as for $BF_3.OMe_2$) was postulated for the simplest etherate ($Me_2Al.OMe_2$). A number of infrared and Raman spectroscopic data [6,15] as well as X-ray diffraction [37] indicate an appreciable distortion of the tetrahedron in compounds of this kind. The molecule of triethylaluminium dioxanate has C_{2h} symmetry and the dioxan molecule exists in the chair form [38]. The coordination of the aluminium atom is closer to trigonal than tetrahedral, which can be accounted for by the electrostatic reduction of the electron pairs involved in the Al–C bond.

The coordination compounds of aluminium alkyls with electron-donating molecules, including ethers, readily conduct electricity [3,8,15,39] ($\kappa = 10^{-9}-10^{-7}$ m^{-1} cm^{-1} in solution in hydrocarbons and 10^{-6} in a pure state), which indicates the presence of the ionic complexes $[R_2Al.2OR_2]^+AlR_4^-$ as well as the neutral complex.

2. Methods of Synthesis

Etherates are obtained in high yields by the reactions

$$n\,RMgX + R_{3-n}AlX_n \xrightarrow{Et_2O} R_3Al \cdot OEt_2 + n\,MgX_2 \quad (n = 1-3)\ ^{1,6,7,40-42},$$

$$3LiR_3 + AlCl_3 \xrightarrow{Et_2O} R_3Al \cdot OEt_2 + 3LiCl\ ^{25,43,44}.$$

In principle, various ethers can be used as the solvent and the corresponding etherates can thus be obtained, but only the use of diethyl ether has been described. The etherates R_3Al (R = Me, Et, n-Pr, or n-Bu), [1,7,43,44] iso-Pr_3Al, [41] t-Bu_3Al, [24,25,41] $Al(CH_2SiMe_3)_3$, [42] and optically active tri-2-methylbutylaluminium etherate [5] have been obtained in this way.

The etherates are usually obtained by mixing trialkylaluminium with ether (exothermic reaction)—this was the method used to synthesise the adducts of Me_3Al, [17,18,29,36,45] Et_3Al, [18,20,21,46-48], and iso-Bu_3Al [22,46,48] with a series of dialkyl, alkylaryl, and cyclic ethers as well as $Et_2AlCH_2X.OEt_2$ (X = Cl, Br, or I) [49] and $(n\text{-}C_{10}H_{21})_3Al.iso\text{-}OPr_2$. [7]

When the etherate is acted upon by another ether which is a more powerful electron donor, a new complex is formed. The 2:1 adducts of trimethylaluminium with dioxan [26] and monoglyme [27] as well as compounds of triethyl-, [20,21] tripropyl-, and tributyl-aluminium [50] of various ethers have been obtained in this way.

According to patent data [5], the etherates of trimethyl- and triethyl-aluminium have been synthesised via the scheme

$$3NaAlR_4 + Al + 3Hg \xrightarrow{THF} 4R_3Al \cdot THF + 3NaHg.$$

A number of etherates have been obtained by adding the etherates of aluminium hydride to olefins on heating under pressure [1,6,7]:

$$AlH_3 \cdot Et_2O + 3CH_2{=}CHR \rightarrow (RCH_2{-}CH_2)_3Al \cdot OEt_2;$$
$$R = H,\ Me,\ Et,\ Pr,\ C_{10}H_{21}\ etc.$$

The above methods are simple in principle, but their application requires the availability of the organometallic compounds. A more convenient procedure involves treatment of alkyl halides in ether with metallic aluminium and magnesium:

$$2Al + 3Mg + 6RX \xrightarrow{ether} 2AlR_3 \cdot ether + 3MgX_2.$$

According to the latest data [51-56], the use of methods described previously [1,7] leads to the cleavage of the ether and the yield of the pure etherate is appreciably reduced [51,52]. Conditions preventing the ether cleavage have been found and triethylaluminium phenetolate has been obtained in 80% yields under these conditions [53,54]. However, a large excess of the ether is used to obtain a liquid reaction mixture and the final solution frequently contains organomagnesium compounds in addition to the OAC. It is more convenient to carry out this reaction in a hydrocarbon medium in the presence of 1.0 mole of ether per gram-atom of aluminium [21,50,55-57]. As a result, there is no need for vacuum distillation. The solution contains only the OAC and can be used directly, for example, in alkylation or polymerisation reactions, which greatly simplifies the experimental technique.

3. Physical and Chemical Properties

(a) Stability. With rare exceptions the etherates are colourless liquids which distil *in vacuo*. Compounds of the type $R_3Al.OR'_2$, where R, R' = Me or Et, can be distilled at atmospheric pressure. The adducts of trimethylaluminium and ethers containing more than one oxygen atom are solid crystalline substances soluble in hydrocarbons.

The heats of formation of the etherates can serve as an indication of their stability. Table 1 shows that, when complexes are formed by aluminium trialkyls with aliphatic ethers, the length of the groups linked to aluminium or oxygen has a small influence on the heat of formation. The stability of the complexes is greatly reduced on passing from aliphatic to aromatic ethers. In benzene [62] and toluene [63] Me_3Al does not form compounds with diphenyl ether. Experiments on the displacement of ethers from etherates [20] showed that the relative stability of the complexes with aluminium trialkyls increases in the sequence $Ph_2O < PhOR < R_2O <$ dioxan $<$ THF $< (PhCH_2)_2O$; if the position of dibenzyl ether is disregarded, this series is consistent with existing ideas concerning the electron-donating properties of ethers [64,65]. The displacement of tetrahydrofuran and dioxan by dibenzyl ether is associated with the high boiling point of the latter. According to ^1H NMR data for Et_3Al etherates at 20°C, the electron-donating capacity of dibenzyl ether is low (as for aromatic alkyl ethers [21]: $Ph_2O < (PhCH_2)_2O \leq PhOR < Bu_2O$. Ethers are readily displaced by nitrogen- and phosphorus-containing electron-donating molecules [26,43,66-69]. Exceptions are known, concerning mainly phenyl-containing donors [6,44,70] and sterically hindered aluminium alkyls [24].

The formation of the etherate stabilises the Al–C bond in straight-chain and branched aluminium trialkyls, which is reflected by a decrease of their tendency towards isomerisation [24] and racemisation [6] and also by an increase of their thermal stability (depending on the nature of the ether and the strength of the Al ← O bond, the decomposition temperature increases by 35–100°C). [22,48]

Apart from certain adducts with aromatic ethers [20,21,48,57,62] and polyethers [6,15,29,33], etherates do not usually dissociate into components. Dissociation is observed only

when the complexes are diluted by hydrocarbons [71]. On heating or irradiation, the etherates are cleaved, but the OAC undergoes further transformations under these conditions. The photochemical cleavage of etherates derived from aromatic ethers, aromatic alkyl ethers, and dioctyl ether [72] as well as thermal cleavage of etherates derived from dimethyl [53], diethyl [6,24], allyl propyl [17], and allyl phenyl [58] ethers, anisole [21,53-56,73] and its substituted derivatives [53], phenetole [21,53,54], diglyme [29], chlorex [58,74], tetrahydrofuran [24], and other cyclic ethers [4,75-77] have been described. The following reactions are therefore used to convert the etherates into free aluminium trialkyls [5,6,41]:

$$R_3Al \cdot OR_2 \xrightarrow[-R_2O]{BF_3 \cdot R_2O} R_2AlF \xrightarrow{RLi} R_3Al$$

$$R_3Al \cdot OR_2 \xrightarrow[-R_2O]{KF} (R_3Al)_2 \cdot KF \rightarrow AlR_3 \cdot KF + R_3Al \quad (R_3Al \cdot OR_2)$$

$$R_3Al \cdot OR_2 \xrightarrow{AlCl_3} R_2AlCl \cdot R_2O \xrightarrow[-R_2O]{LiH} R_2AlH \xrightarrow{olefin} R_3Al$$

$$R_3Al \cdot OR_2 \xrightarrow[-R_2O]{Na} NaAlR_4 \xrightarrow{AlCl_3} R_3Al \ .$$

Table 1. The heats of formation of the etherates R_3Al.ether in solution.

R	Ether	$-\Delta H$, kcal mole^{-1}*	Refs.
Et	Bu_2O	20.0	3,58
Et	$(C_7H_{15})_2O$	18.9	58
Et	$(ClCH_2CH_2)_2O$	16.3	58
Et	PhOEt	14.2	58
Et	Ph_2O	10.2	58
Et	$CH_2(OMe)_2$	31.5**	31
Et	1,4-dioxan	35.3**	31,58
Et	m-$(MeO)_2C_6H_4$	13.4***	31
Et	m-$(MeO)_2C_6H_4$	25.0**	31
Et	$EtO(CH_2CH_2O)_2Et$	18.0***	31
Et	$EtO(CH_2CH_2O)_2Et$	48.0****	31
Et	$MeO(CH_2CH_2O)_4Me$	77.3*****	31
Pr	Et_2O	19.5	59
n-Bu	THF	22.5	59
iso-Bu	THF	22.6	60
C_8H_{17}	Bu_2O	19.0	3

*Taking into account the energy of dissociation via the mechanism $R_6Al_2 \rightarrow 2R_3Al$. [59-61]
**2 : 1 adduct. ***1 : 1 adduct. ****3 : 1 adduct. *****5 : 1 adduct.

The free R_3Al can be isolated from the etherate also with the aid of transolvation with ethers of polyethylene glycols and subsequent thermal dissociation of the complexes formed [6,15].

(b) Physicochemical constants. More or less complete sets of physical properties (boiling and melting points, heats of evaporation and formation, etc.) are available only for isolated examples of aluminium trialkyl etherates [15,45,78]. The simplest constants, such as specific gravity and refractive index, are rarely encountered in the literature [22]. A large number of etherates have been described in the studies quoted (Tables 2 and 3); only the most typical examples are presented here.

In addition, there is some information about the infrared [6,15,18,26,27,36,79,80], NMR, [13,19,39,63,71,81-87] and NQR [88] spectra, luminescence spectra [32], electrical conductivity [22,28,39,59,82], magneto-optical properties [46,89,90], optical rotation [23,91,92], inversion [93,94], dipole moments [3,65], and thermodynamic characteristics [51,78,95-99].

Table 2. The properties of tri-isobutylaluminium etherates.

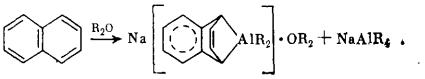
Ether	B.p., °C (mmHg)	n_D^{20}	d_{20}^4	Temp. of onset of decomp., °C	References
Et_2O	88 (2)	—	0.837	155	46, 48
iso- Pr_2O	59—60 (1.5)	1.4519	0.829	—	22
Bu_2O	103—105 (2)	1.4469	0.822	135	22, 46, 48
Dioxan	118—119 (1)	1.4620	0.868	—	22
PhOMe	73 (1)	1.4808	0.874	110	22, 48
PhOEt	80—81 (1.5)	1.4790	0.877	90	22, 48

Table 3. The properties of aluminium trialkyl etherates.

Alkyl	Ether	B.p., °C (mmHg)	d_4^{20}	References
Me	THF	54—55 (2)	—	18
Me	PhOMe	87 (2) *	—	51
Me	$(CD_3)_2O$	72—73 (42)	—	36
Et	Am_2O	109—110 (2)	0.825	58
Et	$(C_7H_{15})_2O$	141—143 (2)	0.828	58
Et	PhOEt	88—89 (1)	0.880	58
Et	Dioxan	111—113 (1)	—	20, 21, 48
Et	Cyclohexyl ethyl ether	90—91 (1)	—	20, 21, 56
Et	$(MeOCH_2)_2$	116—117 (2.5)	—	47
Pr	Bu_2O	103—107 (1.5)	—	21, 50
Pr	PhOEt	115—118 (5)	—	21, 50
Bu	Bu_2O	129—132 (2)	—	21, 50
Bu	PhOEt	123—126 (2)		21, 50
Me_3SiCH_2	Et_2O	64 (0.02)	—	42

*Colourless needles at −78 °C.

(c) Reactions with inorganic compounds. Me_3Al does not usually react with alkali metals, but in the presence of ether or tetrahydrofuran (THF) the reaction proceeds smoothly with formation of $MAlMe_4$. [5] Other R_3Al readily react both in ether and in a hydrocarbon. The etherates react in a very unusual manner with alkali metals or magnesium in the presence of unsaturated hydrocarbons. In this case interesting cyclic OAC are formed together with $MAlR_4$, [100-104] for example:



Free aluminium trialkyls react very vigorously with water (explosively); on the other hand, the corresponding etherates interact quietly [105], particularly in the presence of a solvent, an alkane and aluminium hydroxide being produced. For the molar ratio R_3Al : water = 2 : 1, hydrolysis at room temperature leads to the etherates of alkyl aluminoxanes [106]:

$$2R_3Al \cdot Et_2O + H_2O \rightarrow (R_2Al)_2O \cdot Et_2O + 2RH + Et_2O \ .$$

The yield of tetra-alkylaluminoxanes formed from the etherates is much higher (90%) than in the hydrolysis of free R_3Al (25–30%).

Aluminium trialkyl diethyl etherates begin to react with carbon dioxide at 100–120 °C. The final product is the dialkylaluminium salt, which readily hydrolyses to a

carboxylic acid[24,107-109]. When etherates are treated with CO_2 under pressure, a second Al–C bond is involved in the reaction[6,7]. R_3Al diethyl etherates react with sulphur dioxide to form the corresponding sulphinic acids. The reaction proceeds readily at −50°C via the three Al–C bonds; the yield of highly pure aluminium trisulphinate is quantitative[109,110]. The yields of carboxylic and sulphinic acids in reactions involving etherates are much higher than for ether-free aluminium trialkyls, since the etherates do not undergo side reactions.

Alkali metal hydrides and fluorides (except LiF) react with R_3Al and their etherates to form complexes of the type $M[AlR_3X]$, where X = H or F;[5,6] they do not react with chlorides and bromides. Ethers accelerate the reaction of lithium hydroxide with Me_3Al, which leads, depending on the reactant ratio to $[Me_2AlOLi].AlMe_3$ or $Me_2AlOLi.R_2O$. The ability to accelerate this reaction decreases with enhancement of the electron-donating properties: PhOMe > Et_2O > THF.[111] Triethylaluminium and its tetrahydrofuranate do not react with CaH_2; treatment with BaH_2 leads to $Ba[AlEt_3H]_2$.[112]

On interaction with the acid derivatives of many metals and metalloids, the OAC exchange the organic group for the acid residue with formation of organoelemental compounds:

$$R_3Al \cdot OR'_2 + EX_n \rightarrow ER_n + X_3Al \cdot OR'_2 \ .$$

In these reactions the etherates are as a rule more effective than ether-free aluminium alkyls. The synthesis of trialkylboranes (yield 87–98%),[1,7] alkylmercury compounds (80%),[7,113] dialkylthallium chlorides (57–63%),[7] mixtures of ethylsilanes (85%),[5,6,14] and trialkyl derivatives or gallium[114], antimony, and bismuth[1] has been described. The etherates are particularly effective in the synthesis of alkyl derivatives of phosphorus[6,7], lead[6], and tin[115,116].

Transition metal salts, which do not form stable alkyl compounds, are reduced by etherates to lower-valence compounds or to the free metal[51,117-119]. The reaction proceeds in general at a high rate and to a higher extent than in the case of ether-free trialkylaluminium[21,120-122]. In the presence of stabilising ligands (phosphines, 2,2-bipyridyl, olefins, etc.) it is possible to isolate the intermediates[5,123]. A multiplicity of transition metal compounds have been synthesised in this way, for example: $(Ph_3P)_3Co(N_2)H$;[5] $MeCu(PPh_3)_3.0.5Et_2O$;[124,125] $(Ph_3P)_2Ni.(C{\equiv}CPh)H$;[126] $R_2M(bipy)_2$[125] (M = Fe, Co, or Ni); $(Ph_3P)_4RuH_2$;[5] $MnAl_2Et_4L_4.4THF$;[127] $RCrCl_2.3THF$.[128,129]

The reduction of chromium, molybdenum, tungsten, and manganese salts by aluminium alkyls in an ethereal medium in the presence of carbon monoxide has been proposed for the synthesis of the corresponding metal carbonyls (yield 85–86%),[3] which are otherwise difficult to obtain.

(d) Reactions with organic compounds. In contrast to the free tri-n-alkyl derivatives of aluminium, their diethyl etherates do not add to olefins. However, the etherates of aluminium trialkyls containing branched groups react with ethylene (under certain conditions, the yield of the product is quantitative)[24]:

$$(Me_3C)_3Al \cdot OEt_2 + 3C_2H_4 \rightarrow (Me_3C{-}CH_2{-}CH_2)_3Al \cdot OEt_2 \ .$$

Like aluminium trialkyls, the etherates catalyse the migration of the double bond in olefins when it is present in the centre of the chain[130]. Under the influence of $Et_3Al.OEt_2$, dodec-6-ene is converted into dodec-5-ene and dodec-4-ene. Hex-2-ene isomerises to hex-1-ene with a much higher yield than in the presence of ether-free aluminium alkyls[131]. The etherates inhibit the *cis–trans* isomerisation of straight-chain octenes, which proceeds under the influence of γ-rays in the presence of aluminium alkyls[132]. When ethylene and triethylaluminium are heated together, a mixture of olefins is formed; in this reaction the etherate gives rise predominantly to α-olefins[6].

Etherates react with molecules containing an active hydrogen atom similarly to free R_3Al (with liberation of RH) but more smoothly[5,133-135]. The reactions of etherates with imines[5] and carboxylic[109], thiocarboxylic[136], dithiocarboxylic[137], dimethylarsinic, and dimethylphosphinic[109,138] acids are therefore used to synthesise the corresponding dialkylaluminium derivatives. The reaction of trimethylaluminium with an excess of MeSH in pentane gives rise to $(MeS)_2AlMe$, while in ether the product is $(MeS)_3Al$ in a yield of approximately 100%.[139]

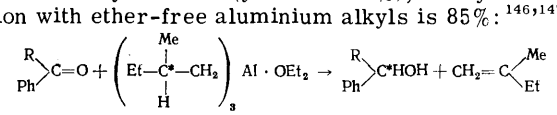
Strong electron donors displace the ethers from etherates, forming complexes with aluminium trialkyls:

$$R_3Al \cdot OR'_2 + D \rightarrow R_3Al \cdot D + R'_2O.$$

A number of such reactions have been achieved, where the donors (D) were NMe_3, PMe_3, and C_5H_5N,[1,7] *N*,*N*,*N*′,*N*′-tetra-alkylethylenediamines[27,66], 2,2′-bipyridyl[26,66,140], 1,10-phenanthroline[26,66], *N*-methylmorpholine and *N*,*N*′-dimethylpiperazine[26], *N*,*N*-dimethylaminomethoxyethane[27], iminotriphenylphosphine[67], R_nEO (E = S, N, or P),[43] and R_3EnPR_3 (E = Si, Sn, or Ge).[44,68,69] The electron-donating capacity of compounds and the rate of displacement decrease in the following sequence[43,68]: $Me_3NO > Me_3PO > Me_2SO > Et_2O$; $Me_3GeNPEt_3 > Me_3GeNPMe_3 > Et_2O \simeq Me_3SiNPMe_3 > Me_2SiPPh_3$.

Aluminium trialkyls in ether do not react with alkyl halides and the reaction with $ClCH_2OMe$ gives a low yield of ethers[141]. In the presence of ether (ether : $R_3Al < 1$) the above reactions proceed readily[74]. Etherates react with CCl_4 to form free radicals and vinyl chloride introduced into this mixture is converted quantitatively into a polymer[142].

The diethyl etherates of R_3Al behave in many instances as effective reducing agents for aldehydes and ketones. Chloral is reduced to trichloroethanol in 89% yield, cinnamaldehyde is converted into ethylstyrylmethanol (95%)[7] and benzophenone is converted into diphenylmethanol (94%).[143] Various alkyl methyl ketones react with $Et_3Al.OEt_2$, forming mainly tertiary alcohols, while free Et_3Al gives a mixture of secondary and tertiary alcohols[144]. The dialkyl etherates of triethylaluminium interact with benzylideneacetophenone via a 1,2-addition mechanism, the yield of the addition product being higher (82%) in the reaction of the di-isopropyl etherate than in the reaction of Et_3Al (69%).[145] The etherates of chiral aluminium trialkyls reduce alkyl phenyl ketones, forming optically active secondary alcohols (yield 91–97%); the yield in the reaction with ether-free aluminium alkyls is 85%:[146,147]



It has been established that, when optically active ethers are used, the aluminium alkyl does not lose the coordinated ligand in this reaction and gives rise to a six-membered transition complex with a pentacoordinate aluminium atom[147]. The nature of the solvent, aluminium alkyl, ether, carbonyl compound, etc. plays a major role in reactions of this type[148-156]. As a rule, on passing to THF and stronger electron donors (amines), the

yields diminish or the reaction does not take place at all [147,153,157-159]. Aluminium trialkyls behave differently in the reactions with anhydrides. The yield of ketene formed from $(CH_3CO)_2O$ increases when the diethyl etherate and particularly the tributylaminate is used instead of free R_3Al. [160]

In a mixture with HCN the etheral aluminium alkyls behave as stereoselective agents for the hydrocyanation of α,β-unsaturated ketones [161-163], for example, cholestenones. The same mixture cleaves the epoxy-groups of steroids, giving high yields of diaxial products. Etherates readily convert epoxyalkanes into the corresponding alcohols [76,150,151]; under certain conditions, triethylaluminium in ether condenses epoxyalkanes to 1,4-dioxan derivatives [164,165]. In contrast to aluminium trialkyls, the etherates interact only insignificantly with the oxygen–oxygen bonds of peroxides [166,167]. The reaction with hydroperoxides [40] proceeds even at 0–20°C, involving the active hydrogen atom and giving rise to organoaluminium peroxides, which are stable in solution for several hours. The diethyl etherate of tri-isobutylaluminium reduces benzonitrile exclusively to benzaldehyde, while free iso-Bu_3Al gives a mixture of the aldehyde and a ketone [168].

III. THE ETHERATES OF ALKYLALUMINIUM HALIDES

With the exception of fluorine-containing OAC, which do not form complexes with ethers [5,10,41], alkylaluminium halides form etherates with a stronger donor–acceptor bond than do aluminium trialkyls. The tendency towards complex formation increases with increasing electronegativity of aluminium: $Et_3Al < Et_2AlCl < Et_2AlBr < EtAlCl_2$. Using the ^1H NMR, [83] cryoscopic [62], conductimetric, and calorimetric [87] methods, a somewhat different OAC acidity series was found: $Et_2AlCl < Et_3Al < EtAlCl_2$; this is associated with the fact that Ph_2O is too weak a base to cleave the diethylaluminium chloride dimer. Diethylaluminium bromide and iodide, which exhibit a greater tendency towards dissociation, add to diphenyl ether [21,87].

Synthesis. These complexes can be obtained by the reaction involving a redistribution of ligands between the alkyl derivatives of sodium [3,169], magnesium [1], or aluminium [1,24] and aluminium halides in ether, for example:

$$n\,RNa + AlCl_3 \xrightarrow{Et_2O} R_nAlCl_{3-n}\cdot OEt_2 + n\,NaCl\ ;$$

$$n\,R_3Al + AlCl_3 \xrightarrow{Et_2O} R_nAlCl_{3-n}\cdot OEt_2\ ;$$

R=Et, Bu, or t-Bu

If the reaction of aluminium with alkyl halides is carried out in ether, a mixture of etherates is formed [21,57]:

$$2Al + 3RX \xrightarrow{R'_2O} R_2AlX\cdot OR'_2 + RAlX_2\cdot OR'_2\ .$$

Higher alkyl halides are cleaved during the synthesis [6,8]. Since ethers retard the cleavage reaction, it is possible to synthesise propyl- and butyl-aluminium sesquichlorides [5], propyl- and isopentyl-aluminium sesqui-iodides, and octyl-aluminium sesquibromides [1] in diethyl ether. Hydrocarbon solutions of diethylaluminium bromide and diethylaluminium iodide etherates have been obtained in 65–90% yield and by the reaction [21,55-57]:

$$2Al + Mg + 4EtX + 2D \rightarrow 2Et_2AlX\cdot D + MgX_2\ ;$$

D = Ph_2O, MeOPh, or EtOPh.

A number of etherates of alkyl aluminium halides have been synthesised by mixing the components and subsequent distillation [15,16,18,48,170] or crystallisation [29,171,172]. In the synthesis of their components account must be taken of the tendency of alkylaluminium dihalides towards disproportionation [173-175]; this tendency increases in the sequence $RAlI_2 < RAlBr_2 < RAlCl_2$: [172,174]

$$2RAlX_2 + \text{ether} \rightarrow R_2AlX + AlCl_3.\text{ether}.$$

The optimum Al : ether ratio can be various and is determined by the nature of the ether [6,172,176]. In this connection it was impossible to obtain the diphenyl etherate [176] and dioxanate [172] of ethylaluminium dichloride in paraffinic hydrocarbons. The dioxanates of ethylaluminium dihalides can be readily obtained from ethylaluminium sesquihalides [172]:

$$2Et_3Al_2X_3 + C_4H_8O_2 \rightarrow [EtAlX_2]_2\cdot C_4H_8O_2 + 2Et_2AlX\ .$$

The formation of Et_2AlX disproves the possibility of disproportionation. The method is of interest, because it makes it possible to obtain the individual compounds from the readily available mixture of alkylaluminium halides.

Table 4. The properties of alkylaluminium halide etherates*.

Etherate	B.p., °C (mmHg)	Other properties	References
$Me_2AlCl\cdot Et_2O$	73–74 (2.5)	—	18
$[Me_2AlCl]_2\cdot[MeOCH_2CH_2]_2O$	—	m.p. 75°	29
$Cl_2AlCH_2AlCl_2\cdot 2Et_2O$	—	m.p. 34–37°	171
$Et_2AlCl\cdot Et_2O$	92–93 (3.5)	d_4^{20} 0.9403	18, 170
$Et_2AlCl\cdot PhOMe$	86 (2)	decomp. temp. 135°	48
$[Et_2AlCl]_2\cdot C_4H_8O_2$	143–146 (3)	m.p. 97–98°	172
$EtAlCl_2\cdot Et_2O$	100–105 (3)	d_4^{20} 1·0779	18, 170
$[EtAlCl_2]_2\cdot C_4H_8O_2$	135–137 (2)	m.p. 118–120°	172
$Et_2AlBr\cdot Ph_2O$	102–106 (4)**	—	21, 56, 57
$[Et_2AlBr]_2\cdot C_4H_8O_2$	—	m.p. 123°	172
$EtAlBr_2\cdot C_4H_8O_2$	—	m.p. 28–30°	172
$Et_2AlI\cdot PhOMe$	99–102 (0.5–1)**	—	21, 56
$Et_2AlI\cdot Ph_2O$	104–105 (1)**	—	21, 56, 57
$[Et_2AlI]_2\cdot C_4H_8O_2$	—	m.p. 127–128°	172
$Et_2AlI\cdot C_4H_8O_2$	—	m.p. ~ 10°	172
$EtAlI_2\cdot C_4H_8O_2$	—	m.p. 46–48°	172
$Bu_2AlCl.Et_2O$	128–130 (0.5)	—	169
$t\text{-}Bu_2AlCl.0.7Et_2O$	70 (10^{-3})	—	21

*The boiling points quoted by Gallais [46,170] (see also Alpatova et al. [15]) are somewhat high compared with the data of other workers.

**With decomposition.

Properties. The majority of the compounds obtained are colourless liquids which can be distilled *in vacuo* and which do not ignite in air; the 2 : 1 complexes with dioxan and monoglyme are crystalline substances (Table 4). According to cryoscopic measurements [18], the etherates of alkylaluminium halides are monomeric. The 1 : 1 compounds of methyl- and ethyl-aluminium halides with di- and poly-functional ethers (dioxan [172], diglyme [29]) are more stable than the R_3Al compounds, and on heating *in vacuo* they split half the ether and are converted into 2 : 1 complexes. Diethylaluminium chloride adds to polyethylene glycol up to the ratio Al : O = 1 : 1, the organic molecule passing from the skew to the transoid conformation in the process [177-179]. 2 : 1 complexes are also

formed under certain conditions [178]. Owing to the presence of the CH_3 side group, polypropylene glycol is incapable of being fully "saturated" by the acceptor. The methylenealuminium compounds $C_2Al-CH_2-AlCl_2$ and $Cl_2Al-CH_2-Al(Cl)-CH_2-AlCl_2$ form complexes with two and three diethyl ether molecules respectively [171,180-182]; on heating above 120°C *in vacuo*, these complexes split off part of the ether with simultaneous disproportionation and polymerisation [171]. The physical properties of the etherates of alkylaluminium halides have been investigated to an even lesser extent than for the etherates of R_3Al. Apart from the data presented in Table 4, there is isolated information about the heats of formation [3,87,177,178], infrared spectra [15,18,178,179], NMR spectra [13,83,171,181-183], and magneto-optical properties [170].

The etherates of alkylaluminium halides show a tendency towards rupturing the C–O ether bond with liberation of the alkyl halide and the formation of alkoxy-compounds of aluminium. Allyl [184] and alkyl phenyl [53-56,73,118] ethers are particularly readily cleaved, while dialkyl ethers [53] and diglyme [29,185] are cleaved with more difficulty. The "stabilising effect" of dialkyl ethers is therefore less pronounced than in the case of R_3Al (the Et_2AlCl decomposition temperature increases from 160° to 170–180°C on formation of the complex with Bu_2O and Et_2O; on the other hand, alkyl phenyl ethers reduce this temperature to 130–135°C [48]). The tendency towards cleavage in the series of aluminium alkyls increases with increase of their acidity: $R_3Al < R_2AlX < RAlX_2$, [73,184] while for different X the tendency increases in the sequence $Cl < Br < I$. [21]

In contrast to free R_2AlCl and $RAlCl_2$, the diethyl etherates of alkylaluminium chlorides do not react with ethyl chloride and vinyl chloride [186], while their reaction with NaF and LiH (in the case of $R_2AlCl.Et_2O$) results in the formation of dialkylaluminium fluorides and hydrides respectively [1]. Alkali metals dehalogenate the etherates of R_2AlCl, sometimes with the cleavage of the ether and liberation of aluminium. The presence of aromatic hydrocarbons rules out side processes, which leads to the formation of the etherates of aromatic alkyl compounds of aluminium [6,187,188]. The etherates of alkylaluminium halides react with tin dichloride and tetrachloride to give a high yield of dialkylstannanes [189] and tetra-alkylstannanes [115] as well as dialkyltin dichlorides [6]. These etherates are used to synthesise various aluminoxanes [106, 190,191], including aluminosiloxanes [192]:

$$2R_2AlCl \cdot Et_2O + H_2O \rightarrow (RAlCl)_2O \cdot Et_2O + 2RH + Et_2O \ ;$$
$$R_2AlCl \cdot THF + R_2AlOLi \rightarrow (R_2Al)_2O \cdot THF + LiCl \ ;$$
$$RAlCl_2 \cdot Et_2O + 2R_3SiONa \rightarrow (R_3SiO)_2AlR + 2NaCl \ .$$

The interaction of methylenedialuminium compounds with aldehydes in tetrahydrofuran has been suggested as a method of synthesising olefins [193]:

$$RCHO + Br_2Al-CH_2-AlBr_2 \xrightarrow{THF} RCH=CH_2 \ .$$

Styrene, nitrostyrene, and vinylnaphthalene have been obtained in yields of 65, 60, and 80% respectively.

In contrast to hydrocarbon solutions of OAC and pure R_3Al, which give rise to a maximum in electrical conductivity on mixing with electron-donating molecules in proportions of 1 : 1, pure Et_2AlCl and $EtAlCl_2$ mixed with diethyl ether and tetrahydrofuran exhibit a maximum corresponding to the ratio Al-alkyl : ether 2 : 1. [39] On subsequent dilution with a hydrocarbon, the position of the maximum shifts, tending towards the 1 : 1 ratio. These results have not been explained satisfactorily.

IV. THE ETHERATES OF ORGANOALUMINIUM COMPOUNDS OF THE TYPE R_2AlY (Y = H, OR, NR_2, ETC.)

The etherates of these compounds are less stable than those described above; this is due to the competing interaction of R_2AlY molecules with one another, forming extremely stable associated species. Dialkylaluminium hydrides do not form stable adducts with ethers for this reason [62], but the existence of such compounds has been demonstrated by infrared spectroscopy [6,15] and calorimetric measurements [59].

Like the R_2AlH, their etherates readily add to multiple bonds, but in many instances this entails the formation of other products [194-199]. Thus the etheradduct Et_2AlH reacts with hexa-1,5-diene to form the etherate of diethylhex-5-enylaluminium [196]:

$$(H_2C=CH-CH_2)_2 + Et_2AlH \cdot Et_2O \rightarrow Et_2Al(CH_2)_4CH=CH_2 \cdot Et_2O \ .$$

In the absence of ether, a cyclic OAC is formed, giving rise to methylcyclopentane after hydrolysis [197,198]. In the presence of ether 1,1-dimethylindene interacts stereospecifically with di-isobutylaluminium hydride, forming a product with the *cis*-configuration, while in the absence of ether a molar mixture of the *cis*- and *trans*-isomers is obtained [200]. The reaction of the etherates of dialkylaluminium hydrides with alkenylacetylenes proceeds via two pathways: addition (as for the free R_2AlH) and metallation (as for the aminates of R_2AlH). [201] Two moles of OAC add to alkynes of the type HC≡CR in ethers [202,203]:

$$R'_2AlH + HC \equiv CR \rightarrow R'_2Al-CH=CHR \xrightarrow{R'_2AlH} (R'_2Al)_2CH-CH_2R \ .$$

With increasing basicity of ethers, the yield of product rises [203]. In octane and toluene only the first stage of this reaction occurs, while in triethylamine metallation takes place.

The introduction of a donor alters the reactivity of dialkylaluminium hydrides, probably as a result of the loosening of the Al–H bond, which increases with increasing strength of the donor [6,204]. In the absence of an ether, diazomethane reacts more effectively with the less associated R_3Al than with R_2AlH. In the presence of an ether, the Al–H bond is preferentially involved in the reaction [205]. Apparently this is why R_2AlH are frequently used as reductants in the form of etheral solutions. The alkyl and alkyl halide derivatives of certain elements (Be, Si, Sn, etc.) are reduced by dialkylaluminium hydrides in ether to the hydrides of these elements [6,206,207]. The reduction of optically active R_3SiX by the etherate of iso-Bu_2AlH takes place without change of configuration (X = OMe or OPh) or with its inversion (X = F, Cl, or SMe), depending on the nature of X. [208,209]

The diethyl etherate of di-isobutylaluminium hydride reduces epoxides quantitatively to primary and secondary alcohols [210]. The presence of stronger electron donors leads to an increase of the yield of the secondary alcohol, while pure iso-Bu_2AlH gives preferentially the primary alcohol. Di-isobutylaluminium hydride in ether reduces nitriles, carboxylic acids, esters, and *N*,*N*-disubstituted amides [6,211] to the corresponding aldehydes. In the presence of an excess of iso-Bu_2AlH amides are readily reduced to the amines. Ethereal solutions of R_2AlH can be used to hydrogenate nitrogen-containing heterocycles, for example, quinoline [211]. The reduction proceeds much more readily and in a higher yield than in the case of $LiAlH_4$.

On heating, dialkylaluminium hydrides cleave dialkyl ethers[53], tetrahydrofuran[75,212] and other cyclic ethers[75], diglyme[29], anisole[53], phenetole, and benzyl ethyl and allyl phenyl ethers[5,7] with formation of compounds of the type R_2AlOR'. Diphenyl ether[53] is cleaved above 200°C, while α,β-unsaturated ethers[213] are cleaved at temperatures as low as 25–35°C. Iso-Bu_2AlH reacts with alkyl allyl ethers as a rule at the double bond, giving rise to inner complexes[5].

The presence of a bond between aluminium and O, N, P, and S atoms greatly reduces the electron-accepting properties of aluminium alkyls, but does not eliminate the possibility of the formation of complexes by these compounds with ethers in many instances. Compounds having the composition $Et_2AlPPh_2.Et_2O$,[5,6] $Et_2AlN_2.THF$,[214] and several adducts of the type $R_2AlNR'_2$.ether[59,215] have been described. A number of etherates of alkylaluminoxanes (Table 5), which undergo polycondensation with formation of polyalkylaluminoxanes on heating, have been synthesised and characterised (Table 5).

Table 5. Alkylaluminoxane etherates.

Etherate	Yield, %	d_4^{20}	Molecular weight		Refs.
			found	calc.	
$(MeAlCl)_2O\cdot Et_2O$	—	—	444	245	190
$(Me_2Al)_2O\cdot THF$	90	—	—	—	191
$Me_3Cl_2Al_2O\cdot Et_2O$	—	—	237–324	224.5	216
$(Me_2Al)_2O\cdot PhOMe$ *	—	—	—	—	191
$(Et_2Al)_2O\cdot Et_2O$	90	0.8576	248	260	106
$(EtAlCl)_2O\cdot Et_2O$	90	1.0880	268	273	106
$(iso\text{-}Bu_2Al)_2O\cdot Et_2O$	85	0.8766	390	372	106
$[(C_8H_{17})_2Al]_2O\cdot Et_2O$	100	1.1332	—	—	106

*M.p. −50°C.

$(Me_2AlCN)_2.THF$,[214] $Et_2AlBH_4.Et_2O$,[217] $EtAlC_2B_9H_{11}.2THF$,[218,219] $(Ph_3Si)_3Al_2Et_6.8THF$,[220] iso-$Bu_2AlMC_5H_5(CO)_3.C_4H_8O_2$ (M = W or Mo),[221] $Me_2AlOLi.E$ (E = Et_2O, THF, or PhOMe),[111] $R_2AlOM(THF)AlR_3$ (M = Li, Na, or K; R = Me, Et, or iso-Bu),[157,222] and $Et_2AlHNi(CDT).Et_2O$ (CDT = cyclododecatriene)[223] should be assigned to the same class of compounds.

V. THE ETHERATES OF UNSATURATED ORGANOALUMINIUM COMPOUNDS

Unsaturated OAC were discovered comparatively recently. Their synthesis in the form of etherates or aminates constitutes frequently the only possibility of isolating them in a pure form; many studies dealing with compounds of the vinyl, acetylene, allyl, and other series have been published.

The direct proximity of a C=C or C≡C bond to aluminium greatly reduces the electron accepting properties of aluminium alkyls owing to the interaction of the π electrons of the multiple bond with the vacant p orbitals of the aluminium atoms in a second molecule, which leads to the formation of a complex with a relatively high dissociation energy[224,225]. On the other hand, aluminium trialkynyls form very stable etherates, sometimes with two ether molecules[224,226]. This is due to a uniform distribution of electron density in the molecule, as a result of which each individual bond has a low polarity; for this reason, the associated species are unstable and are readily cleaved by ether. The foregoing considerations have been confirmed by infrared[227,228] and ^1H NMR[227–231] spectroscopy.

The principal methods for the synthesis of the etherates of unsaturated OAC involve the interaction of alkyl halides and aluminium trihalides with alkenylmagnesium halides[224,229,230,232], alkenyl-lithium[229,230], or sodium acetylides[224,227,228,233,234] in ether. In addition, the reactions of aluminium with vinyl[224] and acetylenic[3] organomercury compounds as well as complex acetylides of the type $MAl(C\equiv CR)_4$ (M = Li or Na) and $NaAlR_n(C\equiv CR)_{4-n}$ are used[224,226]. The etherates of aluminium acetylides are sometimes synthesised by displacing one ether by another in the sequence $Et_2O \rightarrow THF \rightarrow$ dioxan[227] and also by the exchange reaction of $Al(C\equiv CR)_3$ with triethylaluminium or aluminium trichloride in ether[233]. The synthesis of the etherates of allyl-, crotyl, and propargyl-aluminium sesquibromides from aluminium and the corresponding organic bromides has been described[5,232]. The dibutyl etherate and anisolate of but-3-enylaluminium have been synthesised from the Al/Mg alloy and 1-bromobutene[3] in butyl ether or anisole[232]. A method has been patented for the synthesis of the dioxanates, tetrahydrofuranates, and diethyl etherates of a wide variety of cycloalkenylaluminium compounds by the reaction of aluminium, dialkylaluminium hydrides (or $NaAlR_4$), and a conjugated diene in an ethereal medium[235–241].

With the exception of allyl derivatives[6,229,230,232], the etherates of unsaturated OAC are relatively unstable (Table 6). As a rule, compounds with a double bond are mobile liquids, while acetylides are solid crystalline substances. The triacetylides are monomeric in dioxan, while in benzene the molecular weight of $Al(C\equiv CBu)_3.C_4H_8O_2$ varies with concentration (the association factor of 0.7–1% solutions is 1.3–1.5).[224] The molecular weight of the diethyl etherate of trivinylaluminium corresponds to the monomeric form.

Table 6. Etherates of unsaturated organoaluminium compounds.

Etherate	Yield, %	Properties	Refs.
$(CH_2=CH—CH_2—CH_2)_3Al\cdot Bu_2O$	69	b.p. 113 (1)	232
$(CH_2=CH—CH_2—CH_2)_3Al\cdot MeOPh$	—	b.p. 110–115 (1)*	232
$[CH_2=CH—(CH_2)_3]_3Al\cdot Et_2O$	80	b.p. 96–98 (1)	232
$(PhC\equiv C)_3Al.THF$	90	does not melt	224, 226
$(PhC\equiv C)_3Al.2THF$	85	decomp. > 100°	224, 226
$(C_6H_9C\equiv C)_3Al\cdot Et_2O$ **	47	m.p. 78–81°*	227
$EtAl(C\equiv CBu\text{-}t)_2\cdot THF$	85	liquid, decomp. > 140°	224, 226
$Et_2Al—C\equiv CPh\cdot THF$	96	liquid, decomp. > 120°	224, 226
$HC\equiv C—AlCl_2\cdot$dioxan	87	—	233
$Ph_2Al—C\equiv CMe\cdot Et_2O$	81	m.p. 69–73°*	228

*With decomposition.
**C_6H_9 = cyclohexenyl.

The chemical properties of the etherates of unsaturated OAC are somewhat unusual, but in general they resemble those of the etherates of aluminium alkyls. They are unstable in air and are explosively decomposed by water[228,242]. The dioxanate of the triacetylide[224] is inert with respect to CO_2 up to 100°C, condenses with acetone and mesityl oxide, does not react with dimethyl sulphate and ethylene, but initiates the polymerisation of

olefins in combination with $TiCl_4$.[233] The etherates of unsaturated OAC react with various aldehydes and ketones to give the corresponding alcohols[6,227,228,243-245]. In contrast to the etherates of aluminium trialkyls, the etherates of allylaluminium compounds add readily (at 25 to 100°C) to olefins, forming 1 : 1 adducts[229,230].

By virtue of the electron-accepting effect of the vinyl and ethynyl groups, the polarity of the Al–R bond in compounds of the type $R_2AlC\equiv CR'$ and $R_2AlCR'=CHR''$ diminishes, which entails a diminution of its nucleophilic properties. The vinyl and ethynyl groups are therefore more reactive in the reactions of vinyl- and ethynyl-alkyl mixed compounds with carbonyl compounds[169,226,228,244,246], CO_2, alcohols[226,246], and halogens[246,247], which makes it possible to carry out the reactions selectively with the unsaturated group without affecting the alkyl group. Furthermore, the vinyl group in the compounds $R_2AlCR'=CHR''$ is more reactive than the alkyl group in R_3Al.[246] The reactivity of the ethynyl group depends on the nature of the reactants: the ethynyl group reacts more readily with bromine and isopropyl alcohol, while the alkyl group reacts more readily with iodine and CO_2. The reactivity of the groups usually increases in the sequence alkyl < alkynyl < alkenyl. Compounds of the type $R_2AlC\equiv CR'$ are partly associated even in the presence of an ether, while the ethynyl group is in the bridging position, which lowers its reactivity compared with the vinyl group.

VI. THE ETHERATES OF OTHER ORGANOALUMINIUM COMPOUNDS

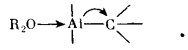
In the first place mention should be made of the etherates of aromatic organoaluminium compounds for which there are about twenty publications. However, since in many chemical reactions (with I_2, alkyl halides, carboxylic acids, metal salts, ketones, aldehydes, nitriles, and esters) these compounds resemble alkyl analogues with rare exceptions (the reactions with α,β-unsaturated ketones[4] and diphenylacetylene[248]) and the data can merely supplement those described above, there is no point in presenting them here.

An extensive class of compounds $M[AlR_4]$.ether, where M is an alkali or alkaline earth metal and R = alkyl, alkenyl, alkynyl, H, OR, etc., is also known. The ether in these compounds is coordinated to the other metal cation and not to aluminium[112,249], but the coordination is significantly influenced also by the group linked to aluminium[224,250]. A series of such compounds, many of which are valuable alkylating and reducing agents, have been obtained and investigated[5-7,15,16,35,224,233,250-253].

VII. THE REACTIVITY OF ETHERATES

When OAC etherates are used instead of ether-free aluminium alkyls in various reactions, the characteristic features of the etherates are manifested: (a) the yield of the desired product is in many instances increased; (b) the reaction frequently proceeds via another pathway and many reactions are characteristic solely of etherates; (c) the reactivity of etherates depends on the strength of the donor–acceptor bond.

It has been shown frequently that coordination of the type of *at*-complexes leads to a weakening of the metal–carbon bonds[254], which is usually attributed to an increase of the amount of their ionic character (the carbanionic mobility of the alkyl groups[15,255-266]), which leads in its turn to an increase of the reactivity of the metal alkyl. An extensive generalisation of this postulate is apparently not feasible, since, together with an increase of the polarity of the Li–C,[256-258] Mg–C,[259,260] Hg–C,[261-263] and certain other bonds[263,264], coordination has been found to entail an acceleration of the homolytic rupture of the Ti–C[267-270] and V–C[271] bonds. Furthermore, it is known that the presence of electron-donating molecules stabilises transition metal–carbon bonds[272,273], but in many instances the opposite effect has been observed[268,274]. The results of ^1H NMR studies on OAC (enhancement of the electropositive nature of the aluminium atom)[63,82,83,275] and of conductimetric studies (a sharp increase of conductivity)[21,22,39] suggest the "ionic loosening" of the Al–C bond:



On the other hand, infrared spectra[30,36,228] and X-ray diffraction[38] indicate only a slight change in the nature of this bond.

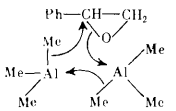
In order to explain processes involving organometallic compounds, it is insufficient to take into account only the polarity of the metal–ligand bond[256,276]. In most cases metal alkyls are associated, the associated species ranging from dimers to hexamers. Coordination to molecules of other compounds, accompanied by changes in the geometry of the organometallic compound, leads to the dissociation of the associated metal alkyls, the nature of which depends on the nature of the alkyls[256,259,277]. Furthermore, many metal alkyls have several comparatively readily accessible vacant orbitals, so that their complexes are capable of being coordinated to the reacting molecule, which results in a decrease of the activation energy in the transition state. Consequently the decisive factor in a particular reaction may not be the amount of ionic character, but the state of the coordination sphere of the metal. Having combined with the electron-donating molecule, the OAC lose or undergo a sharp reduction in their capacity for further coordination (the *d* orbital of aluminium is not readily accessible), so that certain reactions of the etherates of aluminium alkyls are slower or are altogether ruled out. These include primarily the reactions with CO_2, halogens, alkyl halides, H_2S, O_2, olefins, certain carbonyl compounds, nitriles, and all possible ligand exchange processes. However, the decrease of reactivity frequently entails an increase of the yield of the desired product[6,106,107-110,131,144,278]. For example, the presence of an ether or another electron donor has a favourable influence on the alkylation of the salts of various elements by organometallic compounds, which is usually attributed to the enhanced nucleophilic properties of the latter[255]. We believe that a more significant factor in the case of OAC is that the ether neutralises the strong Lewis acid (usually $AlCl_3$) arising during synthesis, reducing its dealkylating and electron accepting capacities, for example[115]:

$$4R_3Al.ether + 3SnCl_4 \rightarrow 3R_4Sn + 4AlCl_3.ether.$$

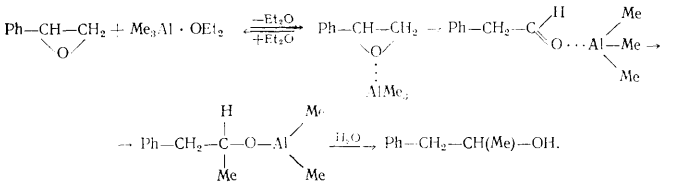
Without the involvement of an ether in this reaction, a mixture of organotin compounds alkylated to different extents is formed, since $AlCl_3$ forms stable complexes of the type $AlCl_3.R_nSnCl_{4-n}$, which prevent further alkylation of tin. This is confirmed by the finding that diphenyl ether, which has only a weak influence on the Al–C bond but forms stable complexes with $AlCl_3$, is effective in this reaction, and this is also true of tetrahydrofuran.

The different types of behaviour of etherates and ether-free OAC are frequently due to the different structures of these compounds[161,167,194,197,198,202,246]. In a pure state and

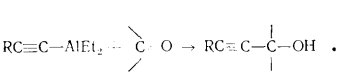
in solution in hydrocarbons aluminium alkyls as a rule exist in a dimeric form [3]. In this form they attack various molecules (aldehydes, ketones, α-olefins, etc.), forming many-centre intermediate complexes [143,148,167,279], for example, the complex of phenyloxiran (styrene oxide) and trimethylaluminium [150,151]:



A further transformation of this complex leads to the primary alcohol $PhCH(Me)CH_2OH$. Etherates, which are saturated monomeric molecules, are effective in such reactions when the ether is displaced by the reacting molecule. The resulting coordination complex reacts further in a manner which depends on the structure of the components. Thus phenyloxiran isomerises to phenylacetaldehyde and, reacting via the carbonyl group, gives rise to a secondary alcohol:

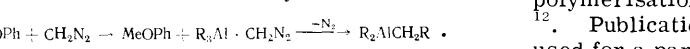


In mixed alkenyl- and alkynyl-alkyl compounds of aluminium the most reactive group (the unsaturated group) is in the bridging position in the absence of an ether [225,246] which lowers its reactivity. In complex formation the reactivity of the unsaturated group increases, so that, for example, the reactions with carbonyl compounds proceed more effectively in ether than in hexane and benzene [169]:

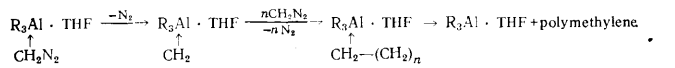


Thus acetone gives the corresponding alcohol in ether with a yield twice as great as in a hydrocarbon, while 2-methylcyclohexanone gives 96% of 2-methyl-1-propynylcyclohexanol in THF and 87% in benzene.

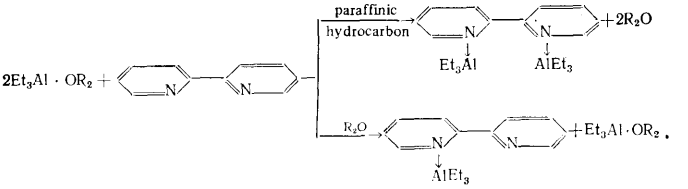
The properties of the whole class of various OAC etherates cannot be judged on the basis of individual instances (for example, $Et_3Al.OEt_2$). Apart from all other factors, the properties of etherates depend on the strength of the Al ← O bond [12,21,151]. For example, on reacting with the anisolate of R_3Al, diazomethane displaces anisole and the resulting adduct rearranges as in the case of the ether-free aluminium alkyl [205]:



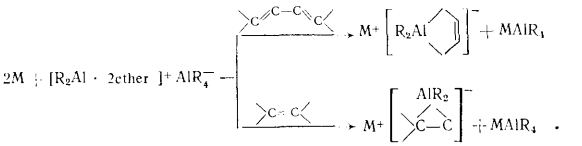
The reaction with $R_3Al.THF$ takes place differently, because tetrahydrofuran is a stronger donor than diazomethane. As a result, diazomethane coordinates via the free *d* orbital (the fifth coordination site of aluminium) with its subsequent polymerisation via the mechanism



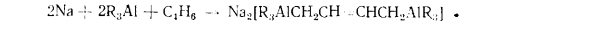
Apart from the strength of the donor–acceptor bond, the reactivity of etherates is influenced by the presence of an excess of the ether [7,140]. One must therefore treat with much caution conclusions concerning the reactivity of etherates if the study has been carried out in an ethereal solution. Thus the claim that the etherates cannot be used to synthesise the 2:1 complex of triethylaluminium with 2,2′-bipyridyl has been disproved [140]:



Finally, in connection with the tendency of the etherates of R_3Al to dissociate into the ions $[R_2Al.2ether]^+$ and AlR_4^-, a large group of reactions characteristic of such ions, with participation of alkali metals or magnesium and unsaturated compounds (aromatic hydrocarbons, olefins, and conjugated diolefins), has been observed [100–103]:



Ether-free R_3Al react quite differently, for example, in the case of butadiene we have



In the presence of stronger solvating agents (diglyme, hexamethylphosphoramide) the formation of butadienes polymerisation products was observed.

Thus the difference between the reactivities of etherates and ether-free OAC is due to the following factors: (a) the decrease of the degree of association of the aluminium alkyl; (b) the change in its geometry; (c) the increase in the degree of electrolytic dissociation; (d) the change in the polarity of the Al–C bond; (d) the ability of the ether to bind side products. The results of the reaction may depend on energy of the Al ← O bond in the etherate. Although some of these factors are interrelated and their effects overlap, in many cases individual factors are decisive. The problem of the dominant influence of one or several of the above factors must be solved in each specific instance, taking into account the specific features of the mechanism of the given reaction and the structure of the intermediate complex.

VIII. THE APPLICATIONS OF ETHERATES

The application of OAC etherates as components of polymerisation catalysts have been reported in reviews [11, 12]. Publications [48,280–285] recommending that etherates be used for a particular purpose in the polymerisation process have now appeared. The use of Et_2AlCl etherates [286,287] or of an ethereal solution of Et_3Al [288] to polymerise ϵ-caprolactam has been described. The ether adducts of aluminium trialkyls are promising in the polymerisation of epoxy-compounds [289–291], as catalysts [292,293], and as reagents [102] for selective hydrogenation and hydroalumination [200,294].

Etherates are fairly mild alkylating agents and this feature permits their employment in the synthesis of incompletely alkylated compounds of various elements: R_2Sn [189] and $RECl_2$ [295] (E = As, B, or P), the yield being appreciably higher than in the case of ether-free aluminium alkyls. Apart from the examples presented in the preceding sections, the use of the ether adducts of OAC

for the synthesis of organic derivatives of beryllium [14], cadmium [295], boron [14,296], aluminium [297-299], niobium and tantalum [42], and titanium [300] and also for the synthesis of alkylcylcopropanes [301], cyclopentanes [299], a wide variety of olefins [235-239,295], alcohols [4-7,224,239-241,302,303], ketones [4,158,304], and carboxylic, sulphinic, and sulphonic acids and their aluminium salts [5,305,306] is of interest.

Etherates are frequently used as the starting materials in the synthesis of other complexes. Many such examples are known among alkyl [24,26,27,43,44,66-69,140,190,307], alkenyl [232], alkynyl [224,227], and phenyl [308,309] OAC. The free aluminium alkyls can also be obtained from the etherates. It has been shown that iso-Pr_3Al and t-Bu_3Al can be most-simply synthesised from their etherates [41].

The heat treatment of various etherates is used to obtain high-purity aluminium (>99.99%), [310] diethylaluminium arylalkoxides [311], and organoaluminium polymers used as components of rocket fuels [312,313]. The employment of etherates makes it possible to increase the yield and purity of polyalkylaluminoxanes [314]. Finally, the formation of stable complexes by aluminium alkyls with ethers is used for their separation [172,315], analysis [3,105,316], and isolation from various hydrocarbon mixtures [317-321].

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Extraction of Heteropolycompounds and Its Application in Inorganic Analysis

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Data on the extraction of heteropolycompounds published in the period 1965 - 1977 have been reviewed. The principal directions of study and recent achievements in establishing the regular features of extraction and investigating the mechanism of extraction have been examined. Data on the use of extraction to separate and determine elements in inorganic analysis have been given. The bibliography contains 211 references.

CONTENTS

I.	Introduction	502
II.	Factors influencing the extraction of heteropolycompounds	502
III.	Extraction of mixed heteropolycompounds	506
IV.	Extraction of reduced heteropolycompounds	506
V.	Extraction of heteropolycompounds by amines of high molecular weight	507
VI.	Mechanism of extraction	508
VII.	Analytical application	510

I. INTRODUCTION

The extraction of heteropolycompounds is recognised as a reliable method for separating a number of elements and for determining trace quantities in various materials. Up to 1965, a comparatively large amount of experimental material had been published on the optimum conditions for the extraction of molybdenum and, to a smaller extent, tungsten heteropolycompounds (this work has been reviewed[1]). In the last ten years, workers engaged in the extraction of heteropolycompounds have carried out theoretical studies devoted to the establishment of the regular features of the process and the mechanism of extraction, and also applied studies, which have lead to success in the development of methods for separating and determining a number of elements. The development of ideas in the extraction of heteropolycompounds is related to the latest achievements in the chemistry of heteropolycompounds[2-4]. A partial bibliography on problems of extraction can be found in Refs. 5–8. An important contribution to the development of the theory and practice of the extraction of heteropolycompounds has been made by combined schools of research workers[8-126]. The behaviour of heteropolycompounds in non-aqueous and mixed media has been described[28,88,98,127,128,129,130-132]. Methods have been developed for determining traces of elements in highly pure materials[14,25,35,101,117,122,123,133-156].

Until the nineteen-sixties, most studies of the extraction of heteropolycompounds were of an applied nature, and included the results of the empirical selection of the optimum conditions for the extraction of a given heteropolycomplex. In recent years there has been an increase in the number of papers devoted to the systematic study of the influence of various factors on extraction equilibrium, the determination of quantitative relationships, and the calculation of extraction constants. Attention is being paid to the composition of the compounds extracted, the nature of the chemical bonding in these compounds, the stoichiometry of extraction, and processes in the organic phase. Amines of high molecular weight, and other extracting agents, are being introduced in place of the traditional oxygen-containing solvents. A number of papers have been devoted to the extraction of ionic associates of heteropolyacids with dyes of various classes.

In analytical chemistry it is possible to distinguish a trend associated with the development of indirect methods for determining elements. These are based on the extraction of a heteropolycompound and the determination of the element from the concentration of the ligand after re-extraction and decomposition of the complex. A characteristic feature of studies in recent years is the introduction of physicochemical and physical methods in the study of extraction (infrared and NMR spectroscopy, radiometry, and polarography). Many analytical procedures recommend a combination of different methods. Extraction has been combined with chromatographic, luminescent, polarographic, atomic-absorption, and neutron-activation methods to determine and separate elements as heteropolycompounds.

II. FACTORS INFLUENCING THE EXTRACTION OF HETEROPOLYCOMPOUNDS

The extraction equilibrium in a system formed by a heteropolycompound and an organic solvent is determined by many factors operating simultaneously. The principal factors are the nature of the extracting agent, the nature and concentration of the heteropolycomplex being extracted, the nature and concentration of mineral acid in the aqueous phase, the presence of neutral salts, and temperature. The extraction equilibrium is reversible, so that the regular features of the extraction and re-extraction are the same. A universal characteristic of extraction is the equilibrium constant. Unfortunately, there are few experimental data on the determination of extraction constants and distribution coefficients. A number of papers give distribution coefficients (or extraction factors) for a definite acidity of the aqueous phase, and this makes it difficult to compare the data of different authors.

1. Nature of the Extracting Agent

Comparison of the properties and extracting power of more than forty solvents of different classes shows that extraction is influenced to a considerable extent by their

basic strength and dielectric constant, and also by their structure and miscibility with water. Attempts to obtain the dependence of the extraction properties of a solvent on any single factor lead to lack of agreement between the theoretical and experimental extraction series. If only the basic strength of the solvent is taken into account, the theoretical order is: nitrobenzene > methyl isobutyl ketone = methyl ethyl ketone > ethyl acetate > pentyl acetate, whereas the experimental order is: pentyl acetate < nitrobenzene < ethyl acetate < methyl isobutyl ketone < methyl ethyl ketone < isopentyl alcohol < octanol < butanol[77].

The extracting power of a solvent shows a correlation with the solubility of heteropolycompounds in it and the dielectric constant of the solvent. Murata and Kiba[107] divided solvents into three groups: those in which heteropolyacids are sparingly soluble (ϵ = 2–4), soluble (ϵ = 3–8), and highly soluble (ϵ = 5–18).

The relationship between the extracting power and solubility of heteropolycompounds has also been studied by other workers[76] (Table 1). Among oxygen-containing solvents, alcohols have the highest extracting power. They extract all known heteropolyacids, in both oxidised and reduced forms. Alcohols are also the best reagents for the extraction of ionic associates of heteropolyacids with dyes of different classes[17,30]. Cyclic alcohols are better extracting agents than aliphatic alcohols[8]. The action of esters and ketones is more selective. Increase in the length and degree of branching of the carbon chain leads to a decrease in extraction[8,10,90,104,157] (Table 2). The distribution coefficients of reduced molybdophosphoric acid in 1.5 M sulphuric acid solutions for extraction by isomeric alcohols and esters are given below[104]:

butanol	pentanol	butyl acetate	isobutyl alcohol	isopentyl alcohol	isobutyl acetate
279.0	259.3	0.42	70.1	85.1	0.28

Table 1. Distribution coefficients of tungstophosphoric acid between aqueous and organic phases (28 ± 1°C, initial concentration 6.1×10^{-3} M).[76]

Solvent	D	Basic strength*	Solubility, M	ε
o-Dichlorobenzene	$4.1 \cdot 10^{-5}$	—	—	—
Chloroform	$2.0 \cdot 10^{-5}$	—	—	4.8
Carbon tetrachloride	$2.0 \cdot 10^{-5}$	—	—	2.2
Benzene	$2.2 \cdot 10^{-5}$	—	—	2.3
Pentyl acetate	$1.1 \cdot 10^{-2}$	90	0.023	4.8
Nitrobenzene	$3.1 \cdot 10^{-2}$	28	0.0146	34.8
Ethyl acetate	$3.2 \cdot 10^{-2}$	84	0.031	6.0
Methyl ethyl ketone	1.5	77	0.171	—
Methyl isobutyl ketone	0.11	77	0.043	13.1
Octanol	2.2	—	0.073	—
Butanol	2.4	—	0.88	17.1

* The basic strength was measured from the displacement of the CH_3OD band in the infrared spectra.

The addition of an inert solvent to the extraction system decreases the extraction[1,90,94]. The use of solvent mixtures is convenient in practice, since in this case the separation of the phases is more rapid (because of the decrease in the miscibility with water), and the organic phase becomes heavier. In the selection of solvent in analysis, account is taken of the miscibility with water, the absorption of light in a given range of the spectrum, the selectivity, and the possible extraction of the ligand. Sometimes, in addition to the principal extracting agent, a solvent having a high solubility in water is added (acetone, propanediol carbonate[45]) to eliminate emulsified water from the extract. Amines, tributyl phosphate, and dimethyl sulphoxide are used only in mixtures with a diluent, polar or non-polar.

Table 2. Influence of the length of the carbon chain on the extraction ($\lg K_{ex}$) of heteropolyacids by alcohols (pH 1, $HClO_4$).[10]

Alcohol	Mo-P	Mo-Si
Propanol	3.29	—
Butanol	1.85	6.29
Pentanol	1.95	6.29
Hexanol	1.66	6.04
Octanol	0.63	5.64

2. Nature of the Compound Being Extracted

The extraction of heteropolycompounds depends on the nature of the central atom and, to a lesser extent, on the nature of the ligand. The decisive factors are the valency of the central atom (which is related to the charge of the anion) and its size. Extraction decreases with decrease in the valency of the complex-forming atom, that is with increase in the charge of the heteropolyanion (Table 3)[8,10,68,77]. In a series of heteropolycompounds of elements of identical valency, the extraction decreases with increase in the ionic radius of the element. The distribution coefficients of molybdophosphoric and molybdoarsenic acids under identical conditions[67] are given below:

	HCl, M	for Mo-As	for Mo-P
Butyl acetate	1.2	$10^{-2} \times 4.4$	100
Butanol + chloroform	0.35	$10^{-3} \times 1.4$	30

The distribution coefficients and extraction constants for molybdenum and tungsten heteropolyacids having the same central atom are of the same order of magnitude in all solvents studied[67,68,77,78] (Table 3).

Table 3. Distribution coefficients of molybdenum and tungsten heteropolyacids of silicon and phosphorus[77].

Solvent	Mo—P	W—P	Mo-Si	W—Si
Pentyl acetate	$1.9 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$	$2.26 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
Nitrobenzene	0.21	$3.1 \cdot 10^{-2}$	$4.2 \cdot 10^{-3}$	$3.08 \cdot 10^{-3}$
Ethyl acetate	0.23	$3.2 \cdot 10^{-2}$	$8.5 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$
Methyl isobutyl ketone	1.08	0.11	$1.1 \cdot 10^{-2}$	$7.0 \cdot 10^{-3}$
Methyl ethyl ketone	1.58	1.5	0.42	0.18
Isopentyl alcohol	3.7	1.8	$1.1 \cdot 10^{-2}$	$1.06 \cdot 10^{-2}$
Octanol	9.6	2.2	$2.5 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$
Butanol	9.2	2.4	4.28	1.32

Comparison of the distribution coefficients calculated by different workers for specific conditions casts doubt on the above relationships. Under real conditions, however,

the distribution coefficient is influenced by many factors (the stability of the given heteropolycomplex, the nature of the mineral acid, the concentration of the ligand, and temperature), so that the breakdown of the relationships is only apparent (Table 4).

Table 4. Optimum concentration of hydrochloric acid for the extraction of molybdenum heteropolyacids, and their distribution coefficients[6].

Extracting agent	v/v_0	HCl, M	D	v/v_0	HCl, M	D
	Molybdophosphoric acid			Molybdosilicic acid		
Diethyl ether	1.7	1.0—1.3	1.65	1.0	0.1—4.0	0.01
Diethyl ether–pentanol (5:1)	4.2	0.1—1.5	410	4.2	1.5—4.0	410
Butyl acetate	0.3	0.1—1.0	620	1.0	3.0	0.6
Methyl isobutyl ketone	0.3	0.1—1.5	620	7.1	0.1—4.0	710
Chloroform–butanol (4:1)	1.0	0.5—1.5	1.2	1.0	0.1—2.0	0.01
	Molybdoarsenic acid			Molybdogermanic acid		
Diethyl ether	1.0	0.5	1.1	1.0	2.0	0.06
Diethyl ether–pentanol (5:1)	4.2	0.1—1.5	1.1	4.2	1.0—1.4	100
Butyl acetate	1.0	2.0	0.07	1.0	2.0	0.08
Methyl isobutyl ketone	0.3	0.1—1.5	620	1.0	0.1—2.0	620
Chloroform–butanol (4:1)	1.0	0.1—2.0	0.01	1.0	0.1—2.0	0.01

The composition of the heteropolyanion remains unchanged on transfer to the organic phase. This is indicated by the fact that the absorption spectra of aqueous solutions and re-extracts of the heteropolycompounds are identical[76], and is confirmed by chemical analysis of the organic phases[7,76,77], by the isomolar-series method[11], by radiometric measurements[158], and by other methods. The fact that the composition of the heteropolycomplex remains unchanged on extraction has made it possible to detect unsaturated complexes of molybdophosphoric acid, formed under certain conditions. At pH 1, complexes having a ratio Mo : P < 12 (even at a ratio Mo : P = 42 in the aqueous phase), extracted quantitatively by butyl acetate and heptanol, are formed[105]. Solutions of phosphate and molybdenum contain highly coordinated forms (Mo : P ≥ 18), extracted by a mixture of butanol and chloroform[13]. The preferential extraction of unsaturated complexes of phosphorus, silicon, and germanium by butanol, and of complexes having a higher molybdenum content by a mixture of butanol and chloroform, has been confirmed[83,85,87]. In some cases, decomposition of the mixed complexes on extraction and the transfer of the binary compounds to the organic phase have been observed[103,159].

Special comparative studies of the extraction of the α- and β-isomers of heteropolycompounds have not been carried out. It has been reported that there are no significant differences in the extraction of the isomers of molybdosilicic acid by dioctylamine[74] and isobutyl alcohol[129].

3. Nature and Concentration of Mineral Acid

In spite of lack of agreement in published data on the pH at which extraction starts, it can readily be seen that the greater the extracting power of a solvent and the ability of the heteropolycompound to be extracted, the lower the acidity of the aqueous phase at which extraction of the complex begins. It is for this reason that in most studies, the comparative extracting power is estimated from the pH corresponding to the start or completion of the extraction of the heteropolycompound. The dependence of the extraction on the acidity of the aqueous phase is represented in the form of distribution curves obtained by plotting the distribution coefficient D (or the percentage extraction, optical density of the organic phase, etc.) against pH, and also in the form of distribution diagrams obtained by plotting lg D against pH (Figs. 1 and 2). The distribution curve has three sections: in the first section, the extraction increases with increase in the acidity, the second section is the range of optimum extraction (D = const), and in the third section the extraction decreases with increase in the acidity. Published papers do not always give all sections of the distribution curve; most frequently, only the first two are given.

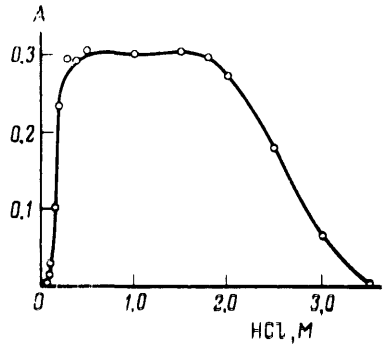


Figure 1. Dependence of the extraction of molybdoarsenic acid by butanol on the concentration of hydrochloric acid in the aqueous phase[67].

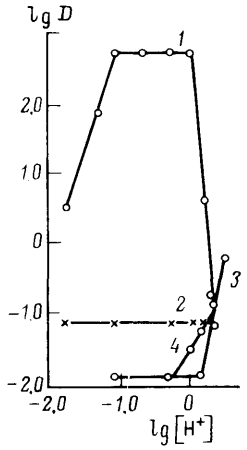


Figure 2. Distribution of molybdenum heteropolyacids between the aqueous phase and butyl acetate[6]: *1*) Mo–P, *2*) Mo–As, *3*) Mo–Si, *4*) Mo–Ge.

The functional pH dependence of the distribution constant on the first section of the curve has the form[1]:

$$\lg D = n \lg [H^+] + \text{const} \ .$$

Using this relationship, some authors attempt to determine the degree of participation of hydrogen ions in the reaction involved in extraction (Table 5). The results are contradictory, and this casts doubt on the justification of determining the number of hydrogen ions by this method. In fact, a priori assumption that the distribution constant remains constant is not completely correct in such a complex system as the heteropolycompound–acid–ligand–solvent system. Simon and Boltz[6] suggest that a correlation cannot be drawn between the slope of the $\lg D$–pH curves and the number of hydrogen ions. This method, which gives good results in the study of the extraction of hydrogen halogenometallates, cannot be used in systems in which, in the opinion of the authors cited[6], the solvent plays a definite role in the formation of the compound being extracted.

Table 5. Experimentally determined numbers of hydrogen ions n taking part in the extraction of heteropolyacids.

Extracting agent	Mineral acid	pH	n	References
Molybdophosphoric acid				
Butanol–kerosene	HCl	1.2—1.5	3	107
Propyl acetate	HNO_3	0.6—1.4	2	9
Propyl acetate	HNO_3	0—0.6	0	9
Butanol, alkyl acetates	$HClO_4$	1—2.5	1	10
Butyl acetate	HCl	1—2	3.3	6
Diethyl ether	HCl	0—1	2.6	6
Chloroform–butanol	HCl	0—1	2	6
Molybdosilicic acid				
Methyl ethyl ketone	HCl	0—2	2	77
Alcohols	$HClO_4$	0—1.5	2	9
Diethyl ether–pentanol	HCl	0—1	3.3	6
Molybdogermanic acid				
Diethyl ether–pentanol	HCl	0—1	3.3	6
Tungstophosphoric acid				
Methyl ethyl ketone	HCl	0—3	1	76
Ethyl acetate, methyl isobutyl ketone, isopentyl alcohol	HCl	0—3	2	76
Nitrobenzene	HCl	0—3	0.5	76

The nature of the anion of the mineral acid has little influence on the first section of the distribution curve, but has a considerable influence on the third section, that is in the range of acidity in which decomposition of the complex takes place. The decrease in the extraction takes place at a lower acidity in sulphuric acid than in nitric acid and other media. This phenomenon is not observed for the extraction of tungsten acids. The difference can be attributed to possible complex formation by molybdenyl ions with sulphate ions[67].

4. Presence of Neutral Salts and Ligand Ions

The influence of added electrolytes on the extraction equilibrium has not been studied systematically. The mechanism of the influence of electrolytes on extraction is not clear. In the opinion of some authors[6,68], the published quantitative characteristics of extraction are greatly distorted, since most measurements have been made at a high concentration of electrolytes, that is in the range in which the discrepancy between the concentration of the components and their activity is considerable. The impossibility of comparing the experimental data obtained by different workers is often due to the difference in the ionic strengths at which the experiments were carried out.

Data have been published on the influence of various ions on the degree of extraction of heteropolyacids in the analysis of specific materials for silicon, phosphorus, and arsenic[106,107,113–116,141,143,144,160]. The mechanism of the influence of neutral salts on the extraction equilibrium is apparently different in each case. Previously, the increase in the distribution coefficients of heteropolyacids at high salt concentrations was attributed to the salting-out effect[1], but recent data show that the influence of sodium, lithium, and caesium salts cannot be regarded as merely due to the change in the ionic strength[76,161–166]. Extracts of heteropolyacids of molybdenum and tungsten with silicon and phosphorus have been found to contain compounds in which the ratio of lithium to the heteropolyanion is 1 : 1.[76] The extraction of molybdophosphoric acid at pH 1–2 is more complete in the presence of sodium, potassium, and lithium chlorides than in their absence, because of the formation and extraction of sodium molybdophosphate having a ratio Na : P = 2.5.[166] Caesium can be extracted quantitatively from solutions of heteropolyacids as a consequence of exchange between caesium ions from the aqueous solution and hydrogen ions of the heteropolyacid from the organic phase[163].

The extraction of salts of molybdenum and tungsten is of particular interest, since all heteropolycompounds are formed and are stable in aqueous solutions only in a definite excess of the ligand ions. It is particularly important to take account of the possible extraction of the ligand in the development of indirect methods for determining an element via the ligand. Isopolymolybdates and isopolytungstates are extracted less effectively than the corresponding heteropolycompounds. Their extraction obeys the same regular features as the extraction of heteropolycompounds[8,105,110,167–169]. Isopolymolybdates are extracted most effectively by alcohols, and least effectively by esters and ketones[7,67,68]. Metatungstate is extracted only by butanol and methyl isobutyl ketone at a concentration of mineral acid $\geq$ 5 M.[68] The distribution of isopolymolybdate between the aqueous and organic phases depends on the nature of the mineral acid, because of complex formation by molybdenum(VI) ions with the anions of mineral acids.

Babko and coworkers[8] introduced the separation factor of molybdenum heteropolyacids and isopolymolybdates, equal to the ratio of their distribution coefficients, and calculated its values in the molybdophosphoric acid–sodium molybdate–solvent system. The greatest separation effect[8] is observed for extraction by esters ($\gamma > 1000$ for propyl acetate at pH 0.2), and the least effective differentiation is observed for alcohols ($\gamma < 50$ in butanol and pentanol). Isopolymolybdates are extracted effectively by solutions of amines of high molecular weight in various diluents[110,167].

5. Time and Temperature

It is considered that shaking a mixture of an aqueous solution of a heteropolycompound with an extracting agent for 1–2 min is sufficient for maximum extraction of the complex into the organic phase under given conditions[7,8,29,66]. It has been reported that equilibrium is established after shaking for 30 s [101] or even 20 s [105,170]. Other studies[66,67] have shown, however, that the percentage extraction of

molybdoarsenic and molybdophosphoric acids increases with increase in the duration of extraction to 30 min. When the extraction mixture is shaken for such long periods, separation of the phases into layers becomes unsatisfactory[170]. It is considered[104] that the time required for extraction equilibrium to be established depends on the initial concentration of the complex in solution. A study of the kinetics of the extraction of α-molybdosilicic acid by trioctylamine in toluene showed that the process is heterogeneous and involves several stages[42].

The influence of temperature on the extraction equilibrium has not been described. The choice of temperature has been determined only by the conditions of formation of the given heteropolycomplex[105].

III. EXTRACTION OF MIXED HETEROPOLYCOMPOUNDS

Considerable attention is being paid to the study of the extraction of mixed complexes, chiefly because of the possible extension of the range of elements whose determination is based on the formation of heteropolycompounds (particularly in the development of indirect methods of analysis), and also because extraction has proved to be an effective method for studying mixed complexes in solution. Mixed complexes are extracted less effectively than the corresponding binary compounds, although the regular features of extraction, noted above, are preserved. The best extracting agents are alcohols and methyl isobutyl ketone[90,104,106,159,171,172]; ethers and esters either do not extract mixed complexes at all or require a high acidity for extraction[31,159,173]. The process is sometimes accompanied by decomposition of the compound[103,159]. Mixtures of alcohols with esters or hydrocarbons extract a complex more effectively, the higher the concentration of alcohol. This is used in analysis to separate mixed complexes from binary complexes[15,47,56,58,60,82]. Trioctylamine extracts mixed molybdenum heteropolyacids quantitatively over a wide range of acidity[35,37].

Extraction depends on the nature and number of atoms replacing the ligand atoms in the coordination sphere. The greatest ability to be extracted is shown by mixed complexes of phosphorus with the maximum number of molybdenum atoms. When molybdenum(VI) is replaced by V(V), W(VI), Nb(V), Th(IV), Ti(IV), and Zr(IV), the ability to be extracted decreases. The extraction of molybdenum complexes of phosphorus decreases in the order Th(IV) > Ti(IV) > Zr(IV), and the form of the curves giving the dependence of the distribution coefficient on the ratio of chloroform and butanol in the extraction mixture is specific for each compound[15]. The greater the metal : molybdenum ratio, the less effective the extraction of the complex[90,159]. In the extraction of the compounds formed in the systems Ge(IV)–Mo(VI)–Cr(III) and P(V)–Mo(VI)–Cr(III), only compounds having a low chromium content are extracted into the organic phase[80,82].

The extraction of a number of mixed complexes of molybdenum and phosphorus has been studied, and the results have been used for the indirect determination of metals[56–58,60,61]. It is considered that the complexes have the compositions P : Nb : Mo = 1 : 1 : 11 for niobium, Ti : Mo = 2 : 11 for titanium, Ce : P = 2 : 1 for cerium, and Th : P = 2 : 1 for thorium. On extraction by alcohols and esters, the thorium and cerium complexes decompose[103], and molybdophosphoric acid passes into the organic phase. The extraction of vanadomolybdophosphoric acid having a ratio P : V : Mo = 1 : 1 : 11 has been most fully studied. The complex is extracted quantitatively by pentanol at pH 0,[48,50] by butanol at pH 1,[60] by methyl isobutyl ketone at pH 0.3,[106] by a mixture of pentanol and diethyl ether[49], and by trioctylamine in various diluents[35,37]. Methyl isobutyl ketone is used particularly frequently. The composition of the complex is preserved on extraction.

Phosphorus compounds are extracted much more effectively than compounds containing other central atoms[100,173].

IV. EXTRACTION OF REDUCED HETEROPOLYCOMPOUNDS

The structures of the yellow (oxidised) and blue (reduced) forms of heteropolycompounds are identical[2], so that it is to be expected that the principal regular features of extraction should be preserved after reduction of the complex.

Unfortunately, it is very difficult to compare published quantitative data, since the distribution data (distribution coefficients, percentage extraction) have been obtained under the optimum conditions for the extraction of the given complex, that is at definite concentrations of the ligand ions, mineral acid, and added electrolytes. This has led firstly to lack of agreement in the results obtained by different workers, and secondly to conclusions which are not fully justified, since the variations in the distribution data are small (under optimum conditions, extraction is practically quantitative) and can be attributed to experimental errors.

Alcohols are recognised as the most effective extracting agents for molybdosilicic acid blues. Isopentyl alcohol is usually employed. Although alcohols having a similar number of carbon atoms in the molecule have a greater extracting power, isopentyl alcohol is sparingly soluble in water, and this is a practical advantage. For molybdophosphoric acid, methyl isobutyl ketone is more frequently used[160,174], in spite of the fact that alcohols have a higher extracting power[7,175,176]. It has been reported that there is a decrease in the molar absorptivity with preservation of a high percentage extraction of acid blues by various oxygen-containing solvents, and that the stability of the complexes in the organic phase depends on the nature of the extracting agent[29,175]. Unfortunately, the works cited do not give the purity of the solvents used, or data on the extent of the oxidation of the heteropolyanion in the organic phase, so that there is some doubt as to whether the decrease in the value of $\bar{\epsilon}$ is due to the partial oxidation of the heteropolyanion blue by impurities in the solvents, particularly since data on the stability of reduced complexes in the organic phase do not always agree[7,176]. Thus the conclusion[175] that the properties of the compound formed in the organic phase depend on the nature of the extracting agent is not completely correct.

The transfer of reduced heteropolycompounds from an aqueous solution to an organic solvent is accompanied by a displacement of the absorption bands in the visible range of the spectrum. The displacement of the absorption maximum is generally hypsochromic (Table 6). In the extracts of heteropolycompound blues reduced by tin(II) salts, a second absorption maximum appears. The reduction products have been divided into two groups, according to their extraction behaviour[7,29]: a) those obtained by the action of "mild" reducing agents (ascorbic acid, 1-amino-2-naphthol-4-sulphonic acid, hydrazine sulphate, p-methylaminophenol sulphate), for which the spectrum of the extract gives one absorption maximum; and b) those obtained by the action of tin(II) salts, for which the spectra

of the extracts contain two absorption maxima. The position of the absorption band is independent of the extracting agent. It has been reported, however, that the absorption spectra of molybdophosphoric acid blues depend on the extracting agent[176]. The α- and β-isomers show different behaviour on extraction[29].

Table 6. Positions of the absorption maxima (nm) for reduced heteropolyacids in aqueous solutions and extracts after extraction by butanol.

Hetero-polyacid	Tin(II) salts		Ascorbic acid		1-Amino-2-naphthol-4-sulphonic acid		Hydrazine sulphate		Refs.
	water	butanol	water	butanol	water	butanol	water	butanol	
α-Mo—Si	740	630 and 720	720	720	—	—	790	720	32
β-Mo—Si	800	630 and 720	800	780	805	800	825	805	32
Mo—P	740	625 and 725	825	780	825	780	825	780	7
Mo—Nb—P	700	730	—	—	—	—	—	—	104

Amines of high molecular weight extract reduced heteropolyacids more effectively than oxygen-containing solvents[24,33]. Thus molybdosilicic acid blue is extracted quantitatively by trioctylamine at pH 1–1.6. The extraction is accompanied by a displacement of the absorption maximum; the magnitude of the displacement depends on the diluent and the nature of the heteropolyacid, but is independent of the nature of the amine[24,26]. Reduced mixed heteropolycompounds are extracted less effectively than the binary compounds.

In analysis, use is made of the extraction of heteropolyacids reduced in aqueous solution, and also of a heteropolycompound in the organic phase after its extraction in the non-reduced form[69,91-93,95,113,115,122-124,133,134,138,141,143,146,147,149,152-156,177-179]. Although the last procedure is more widely used, the process of reduction in organic solvents has been very little studied. The reduction of heteropolycompounds is more difficult in the organic phase than in aqueous solution. The use of tin(II) chloride, mixtures of iron(II) chloride[180] with ascorbic acid[137], and ferrocene[154] have been recommended.

In the reduction of the isomers of molybdosilicic acid, the formation of two-electron blues of β-molybdosilicic acid, and two- and four-electron blues of the α-isomer, has been observed in extracts obtained using dioctylamine in chloroform[73]. In the opinion of the authors cited[72], the four-electron β-isomer can exist only in aqueous solution, and not in the organic phase. Similar results were obtained in a study of the reduction of the isomers of molybdosilicic acid in oxygen-containing solvents[72]. The formation of intermediate products of the reduction of the α-isomer, containing tin(IV) as hetero-atom, is assumed[72].

The polarographic behaviour of heteropolycompounds in organic solvents has been studied in most detail. It is difficult to compare the results of polarographic studies by different workers, since the experiments have been carried out under different conditions (supporting electrolyte, nature of the electrodes, and solvent). The magnitude of of the reduction potential and the intensity of the signal are influenced by many factors, but the mechanism of their action is not clear[53,69-73,91-96,99,111,112,122,123,179,181].

V. EXTRACTION OF HETEROPOLYCOMPOUNDS BY AMINES OF HIGH MOLECULAR WEIGHT

The extraction of heteropolycompounds by amines has been comparatively little studied[24,33-42,72-75,109-172,182-185]. The use of amines is extremely promising in analysis, since the presence, in the molecule of the extracting agent, of the nitrogen atom, which is more basic than the oxygen atom, ensures the quantitative extraction of the elements as the heteropolycompounds. It is true that this is accompanied by a decrease in the selectivity of extraction. The theoretical study of the extraction of heteropolyacids as ionic associates is of interest. Amines in which the hydrocarbon chain contains less than seven carbon atoms are not used, because of their ready miscibility with water. Primary amines extract heteropolyacids with the formation of precipitates, which float at the interface between the phases, particularly in non-polar diluents. The formation of precipitates is also observed in extraction by secondary and even tertiary amines at low concentrations. In the opinion of some authors[24], secondary amines are better extracting agents than tertiary amines.

Extraction by amines is carried out over a wide range of acidity, restricted only by the protonation of the amine and the stability of the heteropolyanion. The extraction of reduced forms begins at a higher acidity[24,33]. The extraction without acidification, reduction of the heteropolycomplex by trioctylamine is observed[39]. The reduction of molybdophosphoric acid by other amines in sulphuric, perchloric, and hydrochloric (but not nitric) acids has been observed by Ivanov[182]. In the extraction of heteropolyacids by insufficient quantities of an amine in diluents having a low polarity, extraction of the complex in quantities greater than that corresponding to the stoichiometry of the ionic associate formed is observed[34]. This effect, which is characteristic of all strong acids, is probably due to the extraction of additional molecules of the heteropolyacids by the compound extracted.

No significant differences are observed in the extraction of the isomers of molybdosilicic acid[35,74]. The composition of the coordination sphere of the heteropolycomplexes remains unchanged on extraction. In the extraction of molybdoarsenic acid from hydrochloric acid solution, however, the ratio of the number of central atoms to the number of ligand atoms is 1 : 11.[74] It was suggested[74] that two forms of complex are extracted: a saturated form having a ratio As : Mo = 1 : 12, and an unsaturated form having a ratio As : Mo = 1 : 9. At the interface between the phases, the colourless unsaturated complex is partly converted into the yellow saturated complex.

The compounds formed on extraction are ionic associates[34,109]. The compositions of the products extracted correspond to the complete replacement of the protons in the non-reduced forms[34,37,109,182]. Fractional amine : heteropolyacid ratios have been found[74], however (from saturation curves). This is attributed to the possible existence of different protonated forms of the complexes in the strongly acidic media in which the experiment was carried out.

The nature of the absorption spectra of the organic phase is independent of the nature of the amine. In the opinion of some authors[24], the position of the maximum in the spectra of extracts of reduced molybdophosphoric acid depends on the reducing agent and the solvent used to dilute the amine.

The mechanism of the extraction of heteropolycompounds as their associates with dyes and quinolinol is probably similar to that for extraction by amines. Heteropolyacids

react with basic organic compounds (generally containing a nitrogen atom in the molecule) to give products sparingly soluble in water. From the nature of the bonding, they can be regarded as ionic associates. In some cases, these compounds dissolve in organic solvents which are immiscible with water, that is it is possible to extract the heteropolycomplex as ionic associates with organic bases (various types of dye, 8-quinolinol). The use of dyes as extracting agents in analysis is promising, since most dyes have high molar absorptivities. The compounds of molybdophosphoric acid with a number of dyes (Crystal Violet, Methyl Violet, Malachite Green, Iodine Green, Safranine, Rhodamine, etc.) are extracted by hydrocarbons, alcohols, and ketones[17,18,22,23,25,59]. The compounds of molybdosilicic acid with dyes of the triphenylmethane, xanthone, and antipyrine series are also soluble in alcohols and ketones, but are not extracted by hydrocarbons and nitrobenzene[30]. Molybdoarsenic acid reacts with dyes to form compounds which can be extracted by alcohols and ketones[16].

Alcohols and ketones, particularly the aromatic and cyclic compounds[17,30], and propyl acetate, are regarded as the best extracting agents for the ionic associates formed by heteropolyacids with dyes. Extraction is sometimes accompanied by flotation at the interface between the phases[30,18]. The extraction of ionic associates takes place in a definite range of acidity, which is broader than that for the extraction of heteropolycomplexes by oxygen-containing solvents. According to some authors[17], the ionic associates of molybdophosphoric acid are extracted at pH 1.3–1.5; according to others[59], the ionic associate of the same acid with Rhodamine B, $[RhB]_3^+[Mo\text{–}P]$, is extracted at the pH of formation of the complex without additional acidification. The same is observed in the extraction of the reduced molybdophosphoric acid by Safranine T.[25] As in the case of extraction by amines, the acidity range is apparently restricted by the stability of the heteropolycomplexes.

The compositions of the compounds formed by molybdosilicic acid with dyes depend on the nature of the dye: the molecule of the molybdosilicic heteropolyacid adds on four molecules of Rhodamine 6G and three molecules of Methyl Violet[30]. 8-Quinolinol also reacts with molybdophosphoric acid to form a compound which is sparingly soluble in water but soluble in oxygen-containing organic solvents[19]. The ability of the compound formed by 8-quinolinol with molybdophosphoric acid to pass into the organic phase decreases in the solvent order[79]: nitrobenzene > carbon tetrachloride > chloroform, that is the order coincides with the order of extraction of the heteropolycomplex in the absence of quinolinol[79]. It is suggested that the compound $[PMo_{12}O_{40}](HOx)_3$, where Ox = 8-quinolinol, is formed.

VI. MECHANISM OF THE EXTRACTION OF HETEROPOLYCOMPOUNDS

Various suggestions have been made regarding the mechanism of the extraction of heteropolycompounds, but the experimental material available up to the nineteen-sixties did not make it possible to give preference to any of these[1]. It is now possible to exclude from the number of hypotheses the suggestion that there is physical distribution of the heteropolycompound between the aqueous and organic phases. The solubilities of heteropolycompounds in water and organic solvents are commensurate, so that the distribution coefficient for a physical distribution mechanism should be ~1, which is not confirmed by experimental data. Experimental observations also do not confirm the hypothesis of an oxonium mechanism of extraction by oxygen-containing solvents, according to which heteropolycompounds are extracted as alkylsubstituted oxonium salts, the so-called etherates. In this case the extraction should take place in a strongly acidic medium, whereas the extraction of heteropolycompounds has been reported even at pH 3–1.

At the present time, two mechanism of extraction, based on the assumption that the heteropolycompound reacts with the extracting agent, are being discussed. According to the donor–acceptor mechanism, extraction is accompanied by the formation of a coordination compound between the molecule of the organic solvent (electron donor) and the heteropolyanion (electron acceptor). The formation of the coordination compound involves the oxygen, nitrogen, or phosphorus atoms of the organic solvent and an atom of the ligand of the heteropolycomplex, in particular molybdenum, which in this case has a coordination number equal to eight. According to the hydrate–solvate mechanism, the reaction of the solvent with the heteropolycompound involves its cationic part. For the extraction of heteropolycompounds by amines of high molecular weight and in the form of compounds with dyes, the ion associate mechanism and anion exchange are also being discussed.

The reaction between heteropolycompounds and the solvent is indicated by changes in the absorption spectra in the visible, ultraviolet, and infrared ranges, and in the PMR and NMR spectra. The spectra of extracts of molybdophosphoric acid show a maximum in the range 308–320 nm;[5,9,109] the same maximum is observed when molybdophosphate is formed in aqueous organic media[28,130]. In the spectra of extracts of tungsten heteropolyacids, the absorption maximum is displaced by 10–15 nm.[68,76,108] In the extraction of the reduced forms, a hypsochromic shift of the absorption maxima in the visible range is observed. The PMR spectra show the chemical shifts and the change in the width of the lines due to water, and also the chemical shifts of the signals of the proton-containing groups of the solvent[83,86,186].

The changes in the absorption spectra are not always interpreted correctly, however. In the opinion of some authors[24,25], the hypsochromic shift of the absorption maximum in the spectra of the extracts of reduced heteropolyacids is due to the donor–acceptor interaction of the molybdenum(VI) atom of the heteropolyanion with the oxygen atom of the solvent. The changes in the spectra might have been due to other factors, however. Thus a change in the oxidation state of the heteropolyanion leads to a change in the absorption spectrum. The products of the attachment of from one to six electrons to molybdosilicic acid differ in the positions and intensities of the absorption band maxima[187]. Differences are also observed in the absorption spectra of the products of the reduction of α-molybdosilicic acid by two and four equivalents of tin(II) chloride or oxalate[29,75].

Changes in the spectra may also be due to a change in the degree of protonation of the heteropolyanion, as shown by a number of workers[188]. The protonation of the sextuply-charged α-molybdosilicate blue leads to a bathochromic shift of the absorption maximum by 60–70 nm, whereas for β-molybdosilicate, a hypsochromic shift of 80–100 nm is observed. Moreover, tin(IV) evidently takes part in the formation of intermediate compounds in the reduction of heteropolycompounds by tin(II) salts. The stabilisation of intermediate mixed compounds may also lead to changes in the absorption spectra of extracts, compared with those of the aqueous solutions. The suggestion

that there is donor–acceptor interaction between the heteropolyanion and the oxygen atom of the solvent, based on the displacement of the bands in the infrared spectra in heteropolyacid–ketone systems[86], was found to be unjustified. It was later shown that the displacement of the bands is due to the formation of new compounds in the system, including alkyl derivatives of benzene[186].

In the opinion of Lebedeva and Vanchikova[83,84,87], evidence in support of the donor–acceptor mechanism of extraction of heteropolycompounds is provided by data obtained in the study of the solvation of molybdenum and tungsten heteropolycompounds of phosphorus, silicon, and germanium by NMR and PMR spectroscopy. According to their observations, the extraction of the heteropolyacids of silicon and phosphorus takes place by different mechanisms. In the presence of an organic solvent, the anionic part of the heteropolycomplex is solvated, whereas in an excess of the solvent, the cationic part is also solvated. The donor–acceptor mechanism has been used[83,84,87] to explain various regular features of the extraction of saturated and unsaturated molybdenum heteropolycomplexes, and also the differences in the extracting power of oxygen-containing solvents. Thus the greater extracting power of alcohols can be attributed to their greater solvating power, since they can act as both electron donor and proton donor; esters and ketones, however, exhibit only electron-donor properties.

Most of the regular features of the extraction of heteropolyacids can be described satisfactorily on the basis of the hydrate–solvate mechanism of extraction of strong acids. The participation of the functional groups of the organic solvents in hydrogen bond formation is indicated by the displacement of the bands due to the stretching vibrations of the OH bonds in butanol and the C = O bonds in propyl acetate towards lower wavenumbers (by 170 cm^{-1} and 40 cm^{-1} respectively) in the infrared spectra of the extracts[9]. In Ivashkovich's opinion[9], the increase in the extraction of molybdophosphoric acid with increase in the acidity of the aqueous phase, that is with suppression of the acidic dissociation of the complex acid, indicates the possible existence of a hydrogen bond between the hydrogen ions of the heteropolyacid and the oxygen atom of the solvent. This gives an associate which is extracted into the organic solvent by a hydrate–solvate mechanism. The formation of an ion pair between the triply-charged anion of molybdophosphoric acid and a solvated hydroxonium ion is assumed by a number of authors[76,77,107,159]. Simon and Boltz draw an analogy between extraction systems of the type iron(III)–hydrochloric acid–organic solvent and the heteropolyacid–organic solvent system; for molybdophosphoric acid, the equation for the reaction involved in extraction should be written in the form[6]:

$$3H(H_2O)\,(S)_x^+ \cdot Cl + [PMo_{12}O_4]^{3-} \rightleftarrows 3H(H_2O)\,(S)_x^+ \cdot [PMo_{12}O_{40}]^{3-},$$

where S represent the solvent.

For the description of the same process, with the assumption that a hydrated heteropolyanion is present in the aqueous solution, Ivashkovich[9] proposed the equation

$$[PMo_{12}O_{40}]^{n-} \cdot m\,H_2O\ (aq) + n\,H^+ \rightleftarrows H_n[PMo_{12}O_{40}]\,m\,H_2O\ (aq) + q\,S \rightleftarrows \rightleftarrows H_n[PMo_{12}O_{40}] \cdot m\,H_2O\,q\,S.$$

A similar equation for extraction has been put forward by other workers[10].

Using the equations for extraction and generally accepted techniques, various authors have tried to determine the solvation number, that is the number of molecules of the solvent taking part in the formation of the ion pair (Table 7). The results are contradictory, and this casts doubt on the justifiability of determining solvation numbers in this case by the usual methods. In fact, in extraction by mixtures of an extracting agent and inert diluents of different composition, the changes in the dielectric constant of the extracting agent are usually not taken into account. It has been shown[78] that the increase in ϵ with increase in the proportion of tributyl phosphate in its mixtures with chloroform leads to an increase in the dissociation of the ion pair in the organic phase, and in the final analysis to a value of the solvation number which is too high. This possibly explains the value of the solvation number, equal to six, found in a study of the tungstophosphoric acid–tributyl phosphate system[189].

Table 7. Experimentally determined solvation numbers m.

Solvent	Medium	m	References
	Molybdophosphoric acid		
Any solvent	HCl	6	91
Propyl acetate	pH 0.3; HNO_3	8	9
	pH 2.0; HNO_3	6	9
Alcohols	$HClO_4$	5	10
Tributyl phosphate		8—9	87
Esters, ketones		0.26—5.3	186
Tributyl phosphate		3	78
	Molybdosilicic acid		
Alcohols	$HClO_4$	8	10
Tributyl phosphate		3	78
		12	87
Dibutyl sulphoxide		6	190
	Tungstophosphoric acid		
Tributyl phosphate	HNO_3	6	189
»		3	78
	Tungstosilicic acid		
Tributyl phosphate		3	78

The values obtained for the solvation numbers, and also the numbers of hydrogen ions involved in the reaction (Table 5), have been used to calculate the extraction constants[10,77–79,97]. The values of the constants found by different authors naturally do not coincide. However, the extraction constants and distribution coefficients found under the same conditions can be used to estimate the comparative extracting power of solvents or the extraction of different heteropolycompounds, so that their determination is undoubtedly necessary.

Various reactions may take place in the organic phase containing extracted compounds, Lakshmanan[77] showed that ion pairs dissociate in nitrobenzene with the removal of the solvated proton. This provides evidence in support of a hydrate–solvate mechanism of extraction.

The differences in the extraction of heteropolyacids having different central atoms are readily explained by the hydrate–solvate theory: the greater the charge of the heteropolyanion, the less effectively it should be extracted. This is confirmed by experimental data (Table 3). The decrease in the extraction of mixed heteropolycompounds compared with the binary compounds can also be understood, in view of the increase in the charge of the heteropolyanion when the molybdenum(VI) atom is replaced by an atom of lower valency (vanadium(V), niobium(V), titanium(IV), etc.). The suggestion that the decrease in

extraction is due to steric hindrance[31] is apparently not fully justified, since the replacement of one atom by another in the coordination sphere has no significant influence on the size of the anion, and the structure of the complex remains unchanged.

Contradictory views have been put forward on the comparative extraction of reduced and non-reduced forms. From the hydrate–solvate mechanism of extraction, a decrease in extraction on reduction should be expected, since the charge of the heteropolyanion increases. According to some authors[19], molybdophosphoric acid blue is extracted more effectively than the yellow form, and this was attributed to a decrease in the acidic dissociation of the compound and a decrease in the hydration of the anion in the aqueous phase. As noted above, however, the conditions under which the extraction of the two forms was studied were not identical, so that in this case, conclusions cannot be reached regarding the comparative extraction of the complexes. The hydrate–solvate mechanism of extraction of heteropolycompounds is confirmed indirectly by the fact that the α- and β-isomers are extracted to practically the same extent (the charges of the two forms are identical).

The same ideas can be used to explain the low value of the extraction factor for isopolymolybdate ions, which carry a high charge (hepta- and octamolybdates). The complex dependence of the distribution coefficient of molybdenum(VI) on the concentration of hydrogen ions and molybdate in the aqueous phase agrees with the suggestion that molybdate solutions contain polymeric species, the composition and charge of which are determined by the concentration conditions and pH.

Extraction by amines can most probably be represented by the following scheme: protonation of the amine, formation of an ionic associate of the heteropolyacid and the mineral acid with the amine (neutralisation), extraction of ionic associates into the organic phase, ion exchange between the mineral acid and the heteropolyacid, and dissociation of the ionic associate in the organic phase. The first attempt to obtain the quantitative characteristics of the extraction equilibrium in a heteropolyacid–amine system was made by workers[109] who determined the composition of the compound extracted in the extraction of α-molybdosilicic acid by tri-iso-octylammonium nitrate in dichloroethane and suggested that the compound is dissociated in the organic phase. From a study of the distribution of the heteropolycomplex between the aqueous and organic phases, they proposed the following equation for the extraction:

$$H_4[SiMo_{12}O_{40}]\ (aq) + 4R_3NHNO_3\ (org) \rightleftarrows \{[SiMo_{12}O_{40}]\ (R_3NH)_{4-n}^{n-}\}\ (org) + n\,R_3NH^+\ (org) + 4NO_3^-\ (aq) + 4H^+\ (aq).$$

From the relationship between the equilibrium concentrations of the components and the stoichiometry of the compound extracted, other workers[109] obtained an equation which made it possible to determine the stoichiometry of the dissociation of the complex in the organic phase, and they calculated the conditional extraction equilibrium constant. According to their calculations, the ionic associate dissociates with the removal of one protonated amine particle; the equilibrium constant depends on the concentration of acid in the aqueous phase, because of the protonation of the heteropolyanion.

Suggestions[109] regarding the nature of the bonding, composition, and behaviour of the ionic associate in the organic phase were confirmed by studies of the extraction of molybdosilicic and vanadomolybdophosphoric acids by trioctylamine in various diluents[34,36,37,41]; infrared spectroscopy and isolation in solid form established that the compounds extracted are ionic. The dissociation of the associates was confirmed conductometrically[36,41].

The nature of the diluent plays an important part in extraction by amines. The extraction is influenced by the dielectric constant and solvating power of the solvent[37,38]. Solvation may involve the cationic part of the heteropolycomplex in the case of a diluent having nucleophilic properties (benzene, toluene), or the anionic part in the case of a diluent having electrophilic properties (dichloroethane). The extraction constant and the distribution coefficient should reflect the overall result of the electrostatic and solvating effects of the diluent and be determined by the contributions made by each. A specific feature of heteropolycompounds is that the charge density on the anion is very low (because of the large size of the anion), so that solvation of the anionic part of the complex has a low probability.

A method has been proposed[182] for calculating the overall constant for the extraction and formation of heteropolyacids by amines, based on published data on the polymerisation of molybdenum(VI) in solution:

$$H_3PO_4 + \frac{3}{2}\,H_4Mo_8O_{26} + 3BHNO_3 \rightleftarrows (BH)_3PMo_{12}O_{40} + 3HNO_3 + 3H_2O,$$

where B represents the amine. No allowance was made, however, for processes in the organic phase.

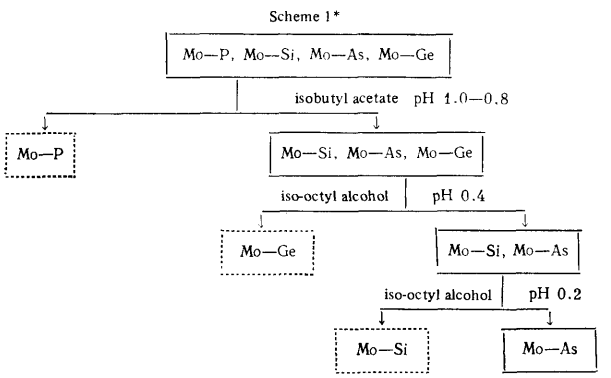
Thus the study of the mechanism of the extraction of heteropolycompounds raises many unresolved problems, and final conclusions regarding the mechanism of the transfer of heteropolycompounds to the organic phase can only be reached using a large amount of experimental material, including the results of kinetic studies of the process.

VII. ANALYTICAL APPLICATION OF THE EXTRACTION OF HETEROPOLYCOMPOUNDS

1. Separation of Elements by Extraction

The greatest number of schemes has been proposed for the separation of phosphorus, silicon, arsenic, and germanium. Methods have been developed for the successive separation of all four elements, the extraction of one of the heteropolyacids in the presence of the others, and the separation of combinations of two or three elements. The distribution diagrams for molybdenum heteropolyacids in oxygen-containing solvents and their mixtures[6] can be used to select conditions for the quantitative separation of many elements (Table 4). Paul[63] put forward a scheme for separating the same elements, based on selective extraction in perchloric acid (scheme 1).

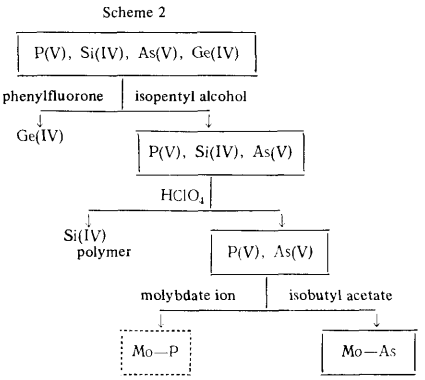
Scheme 1*



† The continuous lines denote aqueous phases, and the broken lines organic phases.

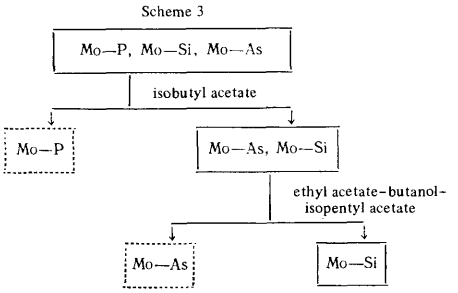
The separation schemes sometimes include reactions not associated with the formation of heteropolycompounds (polymerisation, complex formation by one or several elements, precipitation). Thus a scheme for separating germanium, phosphorus, silicon, and arsenic[64] proposes the separation of germanium as its complex with phenylfluorone, and the conversion of silicon into polymeric forms which do not give a complex with molybdate ions (scheme 2).

Scheme 2



The following scheme has been proposed for separating phosphorus, arsenic, and silicon by varying the extracting agents[191]:

Scheme 3



Amines of high molecular weight are less selective, but it is possible to separate the molybdosilicate complex from 2 M sulphuric acid solution and the molybdophosphate complex from 2 M perchloric acid solution using tri- and dioctylamine in chloroform, in the presence of arsenic and germanium[74].

Methods have been proposed for separating silicon from its mixtures with phosphorus and arsenic by the extraction of the molybdenum complex into methyl isobutyl ketone in the presence of citrate ions, which decompose the phosphorus and arsenic complexes[191], and for separating silicon from arsenic by extracting the molybdosilicate into iso-octyl alcohol[192]. A method has been proposed for separating phosphorus from the same mixture by extracting the compound of molybdophosphate with Crystal Violet into alkyl acetates at pH 0.2–0.5. The extraction is not affected by the presence of unlimited quantities of silicon, or by a tenfold excess of arsenic[8].

A method has been proposed for separating phosphorus from silicon and germanium by extracting the tungsten heteropolycomplex into butyl acetate or its mixtures with diethyl ether from 0.5–1 M sulphuric acid solution[68].

A method has been proposed[124] for separating the corresponding molybdenum heteropolyacids from a mixture of silicon, phosphorus, and arsenic by extracting into isobutyl alcohol at different acidities. Methods for separating pairs of elements (phosphorus and silicon, phosphorus and arsenic, phosphorus and germanium) are based on the ease of extraction of the heteropolycompounds of phosphorus[62,63,105,142,193]. Various methods for separating elements are based on a combination of extraction and the selective decomposition of the heteropolycomplexes in mineral acids[35].

2. Extraction Methods for Determining Elements

Extraction–photometric methods for determining elements are most widespread. This is natural, in view of the high molar absorptivity of heteropolycompounds, particularly the reduced forms (in the visible range) and the mixed complexes. Extraction extends considerably the possibilities provided by the photometric method for a number of reasons: firstly, the element is concentrated; secondly, the unstable isomers of heteropolycomplexes are stabilised; thirdly, the separation from the excess of molybdate or tungstate ions makes it possible to carry out measurements in the near ultraviolet range, where the absorption by the complexes is a maximum; and finally, extraction has provided extensive possibilities for developing indirect methods for the photometric determination of elements via the ligand.

The extraction of molybdosilicic acid by pentanol is used to determine down to 0.02% silicon in copper and brass[150], and by ethyl acetate to determine silicon in sea water[157]. In the extraction of reduced forms, butanol is used to determine down to 5×10^{-4}% silicon in titanium[101], isopentyl alcohol is used to determine silicon in a number of salts, alloys, and steels[113,120], and traces of silicon in antimony, thallium, gallium, and indium[133,134], and a mixture of chloroform and propane-1,2-diol carbonate is used to determine down to 0.2 $\mu g\ ml^{-1}$ silicon in solutions[45]. A number of methods for determining silicon are based on the extraction of the yellow forms of heteropolyacids with subsequent reduction in the organic phase. Extraction of molybdosilicic acid by pentanol with reduction by tin(II) chloride has been proposed for determining silicon in highly pure aluminium[149], extraction by butanol with reduction by a mixture of iron(II) sulphate and ascorbic acid for the determination of down to 2×10^{-3}% silicon in niobium and tantalum[137,138], extraction by methyl isobutyl ketone with reduction by tin(II) chloride for the determination of down to 2×10^{-3}% silicon in vanadium[140] and in solutions of hydrogen fluoride in the presence of tantalum[155], and extraction by isopentyl alcohol with reduction by tin(II) chloride for the determination of traces of silicon in copper and copper alloys[114].

Amines of high molecular weight are being widely used as extracting agents. Conditions have been recommended for the extraction of yellow molybdosilicic acid by a solution of tri-iso-octylammonium nitrate in dichloroethane for the determination of down to 10^{-4}% silicon in solutions[109], by a solution of trioctylamine in toluene for the determination of down to 10^{-3}% silicon in vanadium pentoxide[35], by solutions of di- and trioctylamine in chloroform for the determination of silicon in steels[74], and by a solution of diethylhexylamine in dichloroethane for the determination of down to 1 $\mu g\ ml^{-1}$ silicon in solutions[183]. The extraction of the reduced forms of molybdosilicic acid by amines has also been proposed: by a solution of dioctylamine in pentanol for the determination of down to 0.01 $\mu g\ ml^{-1}$ silicon in solutions[26]; by a solution of trioctylamine in toluene for the determination of silicon in plants and fertilisers[33]; and by a polyethoxylated amine in butanol for the determination of down to 10^{-7}% silicon in pure water[194].

Extraction by isopentyl alcohol of molybdoarsenic acid reduced by hydrazine sulphate is used for the extraction–photometric determination of down to 5×10^{-5}% arsenic in tin, antimony, aluminium, thallium, and indium[133,134,136]. A method involving reduction of the complex by tin(II) chloride after its extraction by a mixture of diethyl ether and butanol, having a detection limit of 10^{-4}% arsenic[148], and also a method for extracting the non-reduced complex by di- and trioctylamine (detection limit 10^{-4}%) and by a number of other amines for the determination of down to 0.04 μg ml^{-1}, [152,184] have been proposed. Arsenic and phosphorus can be determined in tungsten–rhenium alloys[156].

The extraction of molybdophosphoric acid by butyl acetate has been recommended for determining down to 4×10^{-6}% phosphorus in iron[177] and 0.35 μg ml^{-1} in solutions[195], extraction by isobutyl alcohol in mixtures with benzene and ethanol for the determination of phosphorus in solutions containing the products of the deprotonation of adenosine triphosphate[196], and extraction by di- and trioctylamine for determining phosphorus in steels[74]. Most extraction–photometric methods for determining phosphorus, however, used extraction of the mixed vanadomolybdophosphoric acid, and also reduction of the complex in the aqueous phase before extraction or in the organic phase after extraction. Extraction of the mixed heteropolycomplex by methyl isobutyl ketone is proposed for determining phosphorus in steels and alloys[105,144], in ferroniobium, ferrotitanium, and niobium ores[121], in ferrovanadium and ferrous alloys[120], extraction by butanol for the analysis of silicon tetrachloride (detection limit 5×10^{-7}% phosphorus)[133], by pentanol for the analysis of solutions containing down to 1.5 μg ml^{-1} phosphorus[50], and by trioctylamine in toluene for determining down to 10^{-3}% phosphorus in vanadium pentoxide[35].

Reduced forms of molybdophosphoric acid are extracted by mixtures of dioctylamine with pentanol and chloroform in the analysis of solutions with a detection limit of 0.01 μg ml^{-1} phosphorus[26], by isopentyl alcohol for determining down to 10^{-6}% phosphorus in tin[133] and down to 5×10^{-7}% phosphorus in methyltrichlorosilane[139], by methyl isobutyl ketone for the analysis of pure iron, and by butanol and isobutyl alcohol for the analysis of solutions containing down to 0.05 μg ml^{-1} phosphorus[175,176]. Many procedures recommend the extraction of the yellow molybdophosphate complex with subsequent reduction in the organic phase, most frequently using tin(II) chloride. The extraction is usually carried out by alkyl acetates; butyl acetate for determining traces of phosphorus in salts, metals, and alloys[115], and isobutyl acetate[63], ethyl acetate[62,180], and isopentyl acetate[178] for the analysis of iron and steels[147]. Various authors recommended diethyl ether[133], alcohols, and their mixtures with chloroform[141,143,146,177]. A method involving the reduction of the molybdophosphate complex by ascorbic acid in the re-extract after extraction by butanol has also been proposed for the analysis of alloy steels[151].

A number of methods for determining phosphorus in solution are based on the extraction of the ionic associates of molybdophosphate with dyes of different types[12,17,18,25,59].

In addition to traditional extraction–photometric methods, methods based on the reactions of heteropolycompounds in organic phases are now being developed. Titrimetric methods for determining phosphorus and silicon, based on the neutralisation of the heteropolyacids by strong bases in the organic phase with visual[20,21,197] and conductometric indication of the end-point of the titration[198], have been proposed. Phosphorus in natural waters has been determined by flame photometry in sodium molybdophosphate extracts[166] (detection limit 10^{-3} μg ml^{-1} phosphorus). A neutron-activation method has been proposed for determining phosphorus in steels, involving the extraction of molybdophosphoric acid by butanol and measurement of the quantity of ^{32}P ($T_{1/2}$ = 14.3 d) in the re-extracts[145].

A number of methods have been proposed for determining silicon, phosphorus, and germanium in steels, bronzes, and solutions, based on the polarographic reduction of heteropolycomplexes in the organic phase[53,69-71,73,91,92,95,96,122-124,179]. A method has been proposed for determining small quantities of elements from the chemiluminescence of the compounds formed by heteropolyacids with luminol after extraction by solvent mixtures[199,200].

Extraction is also used to determine elements which are not typical complex-forming elements in heteropolycompounds. Thus an extraction–photometric method has been proposed for determining down to 0.04 μg ml^{-1} niobium[104] and antimony[173]. Methods have been developed for extracting caesium by nitrobenzene in the presence of molybdophosphoric acid[162-165]. Extraction can also be used to determine elements which act as ligands in heteropolycomplexes. Methods have been described for the photometric determination of down to 25 μg ml^{-1} vanadium, involving the extraction of vanadotungstophosphoric acid by methyl isobutyl ketone[172] and isobutyl alcohol[201]; for the polarographic determination of molybdenum, involving the extraction of vanadomolybdophosphoric acid by isopentyl alcohol[93]; for the extraction–photometric determination of vanadium in aluminium with a detection limit of 4×10^{-4}%;[171] and for the determination of tungsten, involving the extraction of tungstophosphate[202].

In the last ten years, indirect methods have been developed for determining elements by the formation and extraction of heteropolyacids. These are based on the extraction of the heteropolycomplex under the conditions of minimum extraction of molybdate ions, decomposition of the heteropolycomplex, and determination of molybdenum(VI). The favourable stoichiometric ratio of the central atom and the ligand makes this method extremely promising for decreasing the detection limit (the multiplication factor in most cases is twelve) and extends the range of reagents and methods.

A large number of indirect methods use the photometric version, based on the formation of coloured complexes of molybdenum(VI). The use of the familiar formation of the complex of molybdenum(V) with thiocyanate ion has made it possible to develop methods for determining phosphorus in solutions (effective molar absorptivity 1.56×10^5),[65] and for determining down to 10^{-6}% phosphorus in iodine and highly pure tin[133]. A number of methods, including the determination of down to 10^{-7}% phosphorus in hydrochloric and nitric acids, are based on the kinetic determination of molybdenum(VI).[117-119] The use of organic reagents for determining molybdenum(VI) is particularly effective. Indirect photometric methods involving the use of phenylfluorone[129], azo-compounds[27], 2-amino-4-chlorobenzenethiol[54], benzidine, and gallic acid in the presence of hydrogen peroxide[203] have been proposed. Conditions have been recommended for determining microquantities of phosphorus and arsenic in rhenium using zinc dithiol (effective molar absorptivity 1.7×10^5 for phosphorus and 2×10^5 for arsenic) and Sulphonitrophenol M ($\bar{\epsilon}_{eff} = 4.6 \times 10^5$ for phosphorus and 4.5×10^5 for arsenic)[142].

An indirect titrimetric method with complexometric titration of molybdenum(VI) after the extraction of molybdosilicic acid by isopentyl alcohol with subsequent decomposition has been proposed for determining silicon in silicides[204], and titration of Mo^{III} by permanganate after the reduction of Mo^{VI} in a reductor has been recommended for the analysis of silicates containing up to 68% SiO_2.[205] The intense absorption by molybdenum(VI) in the ultraviolet range of the spectrum is used in a number of methods for determining 0.1 μg ml^{-1} silicon and phosphorus[51], 0.3 μg ml^{-1} germanium[48], and 0.48 μg ml^{-1} vanadium[47].

Methods using atomic-absorption spectroscopy are of particular interest. Atomic-absorption spectroscopy is usually employed for the direct determination of metals. The method is inconvenient for determining non-metals, since the resonance lines of non-metals lie in the far ultraviolet range of the spectrum. In this case it is appropriate to use indirect methods combined with extraction separation from the excess of the element via which the measurement is being made. For example, molybdenum has a resonance line at 313.3 nm; the concentrations of phosphorus, vanadium, and other elements can be determined from the intensity of this line. The indirect method is also used to determine a number of metals which form mixed heteropolycomplexes, extracted under definite conditions.

The method was first used to determine down to 0.015 μg ml^{-1} phosphorus in solutions[125,126]. A number of methods, including descriptions of the conditions of formation, extraction by a suitable extracting agent, decomposition of the heteropolycomplex, and elimination of the co-extraction of molybdenum(VI), were later proposed for determining metals and non-metals. Methods have been proposed for determining silicon, phosphorus, arsenic, and germanium[6], down to 0.01 μg ml^{-1} phosphorus and silicon, and 0.025 μg ml^{-1} arsenic[191]; down to 0.08 μg ml^{-1} silicon and phosphorus[55]; silicon in organic compounds[206,207]; down to 0.005 μg ml^{-1} silicon (including the precipitation of lead molybdate)[46]; down to 0.07 μg ml^{-1} arsenic[52]; down to 0.01 μg ml^{-1} arsenic[191]; small quantities of phosphorus[208], arsenic[209], and germanium[210] in water; down to 0.05 μg ml^{-1} germanium[48] and arsenic in sulphides[211]; and down to 0.5 μg ml^{-1} vanadium in solutions[49] and aluminium alloys[60]. Kirkbright and coworkers proposed a number of methods for determining metals, involving the determination of molybdenum by atomic absorption: niobium[56], cerium[61], thorium[57], and titanium[58]. In some procedures, the direct introduction of the extracts into the flame is recommended, avoiding the operations of re-extraction and decomposition of the complexes[196].

Almost all papers giving specific recommendations for the extraction of heteropolycompounds give data on the influence, on the degree of extraction, of various ions present in the solution at the moment of formation of the complex and its extraction into the organic phase; iron(II), iron(III), aluminium(III), chromium(III), tin(IV), tungsten, and others (a total of ~40 ions). In the present review, however, it is not possible to deal with the results of these studies in detail, and readers are referred to the papers dealing with each specific determination.

* * *

The above review shows that in recent years, considerable success has been achieved in the theory and practice of the extraction of heteropolycompounds: experimental material has been accumulated, making it possible to discuss the mechanism of extraction; the limits of detection of elements by extraction methods have been lowered considerably; and the range of materials and elements extracted as heteropolycompounds has been extended. The mechanism of the transfer of a heteropolycompound from the aqueous to the organic phase has not yet been determined (that is the kinetics of the process have not been studied), however, and there is lack of agreement on the mechanism of formation of the compound extracted. The mechanism of the reduction of complexes in the organic phase is not clear, and the mechanism of the influence of added salts on extraction has not been studied. There are no sufficiently clear-cut practical recommendations on the separation of elements having similar properties at low absolute concentrations, or on the determination of a small quantity of a given element in the presence of large quantities of other elements having similar properties.

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The Use of High-pressure Liquid Chromatography in the Analysis of the Structural Components of Nucleic Acids

V.K.Kagramanova, S.N.Bubenshchikova, and L.A.Baratova

The advances in the analysis of the structural components of nucleic acids by high-pressure liquid chromatography are described and surveyed. The general ideas concerning the requirements imposed on sorbents at the present time in order to increase the efficiency of the chromatographic process are summarised. The methods and the results of the employment of effective ion-exchange sorbents in the separation and ultramicroanalysis of mixtures of the heterocyclic bases, nucleosides, nucleotides, and their derivatives are briefly considered.
The bibliography includes 82 references.

CONTENTS

I. Introduction 517
II. Ion-exchange sorbents used in effective high-pressure liquid chromatography 517
III. The separation of the structural components of nucleic acids by high pressure liquid chromatography 519

I. INTRODUCTION

The development of effective analytical methods plays a decisive role in the study of the structure of nucleic acids. The improvement of the technique of paper and thin-layer chromatography and the use of these methods in conjunction with electrophoretic and radiometric techniques made it possible to increase considerably their sensitivity and resolving capacity[1-4]. However, in view of the complexity and long time required for the application of these analytical methods, the problem of the structural analysis of nucleic acids cannot be regarded as solved.

The introduction into the ultramicroanalytical practice of a special spectrophotometric technique, the use of pumps permitting a low and controlled flow rate, and the preliminary formation of gradients in the capillary[5,6] permitted a successful solution of certain specific problems of the separation and analysis of oligonucleotides with the aid of column liquid chromatography[7]. However, the need to increase the rate of separation and the employment for this purpose of much higher pressures required a modification of the chromatographic technique. The construction in recent years of high-pressure chromatographs equipped with a reliable automatic control system and highly sensitive detecting devices as well as the appearance of new and effective sorbents greatly extended the prospects for the development of the analytical chemistry of nucleic acids[8-10], permitting the use of high-pressure liquid chromatography in the rapid ultramicroquantitative analysis of a wide variety of structural components.

Unfortunately the large-scale practical application of high-pressure liquid chromatography in structural studies on nucleic acids is to a large extent held back by the inadequate, in our view, information about the possibilities of modern ion-exchange sorbents and hence the difficulty of selecting the optimum conditions for a particular analysis. It therefore appears timely and useful to survey and give a systematic account of studies published hitherto concerning the employment of this method in the analysis of the structural components of nucleic acids and also to outline the trends in its development and further prospects for its application.

This review does not deal with the general problems of the theory of chromatography, which have been described in detail in a number of articles and monographs[8,9,11-17].

II. ION-EXCHANGE SORBENTS USED IN EFFECTIVE HIGH-PRESSURE LIQUID CHROMATOGRAPHY

The theory of chromatography developed by Martin and Synge[11], Lapidus and Amundsen[12], Giddings[13,18], and a number of other investigators[19] permits the formulation of the requirements which must be met by the sorbents used in column liquid chromatography and whose fulfilment is necessary for the optimisation of the separation of the components of the mixtures analysed. We shall consider here only some of the principles underlying the theory of high-pressure liquid–liquid chromatography.

According to the Beer–Lambert law, in the region of linear working characteristics of the spectrophotometric detector (used most frequently in column liquid chromatography in the analysis of components of nucleic acids), i.e. under conditions where the detector signal is proportional to the concentration of the absorbing substance in the cell, the optical density A of the substance is specified by the equation

$$A = \lg \frac{I_0}{I} = \varepsilon c l, \qquad (1)$$

where I_0 and I are the intensities of the incident and transmitted radiation respectively, ϵ is the molar extinction coefficient of the substance, and l is the optical path length. For the Gaussian distribution, the maximum concentration of the test substance (c_{max}) in the absence of the "spreading" of the peaks in the detector cell is defined by the expression[19]

$$c_{max} = 4M/w_V\sqrt{2\pi}, \qquad (2)$$

where M is the amount of the substance in moles and W_V the width of the peak expressed in units of volume. Thus the optical density of the substance at the maximum on the distribution curve (A_{max}) is described by the equation

$$A_{max} = \varepsilon l \frac{4M}{w_V\sqrt{2\pi}}. \qquad (3)$$

The highly sensitive spectrophotometric detectors with a small cell volume (down to 8–10 μl) constructed at the present time make it possible to record extremely small (picomolar) amounts of the nucleotide[17]. Detectors of this class ensure a minimal contribution to the peak variance (up to 8%). Consequently the lower limit of the sensitivity, determined by the value of A_{max}, depends on

the "spreading" of the band of the test substance in all the remaining parts of the chromatographic system, in the first place in the chromatographic column.

The efficiency of the chromatographic column, expressed in terms of the number of theoretical plates N or the height equivalent to the theoretical plate H, is related to the peak width as follows[11]:

$$N = \frac{16t^2}{w_t^2} \quad (4)$$

or

$$H = \frac{L}{N} = \frac{Lw_t^2}{16t^2}, \quad (5)$$

where t is the retention time of the test substance on the column, w_t the peak width expressed in units of time, and L the column length (in cm).

The generalised non-equilibrium Giddings theory[12,13] makes it possible to estimate the contributions of the main components of the overall variance, which are due to the turbulent and longitudinal molecular diffusion as well as the resistance to mass transfer. The overall height equivalent to the theoretical plate, equal to the sum of the heights corresponding to the contributions of the above peak "spreading" factors, is

$$H = H_1 + H_2 + H_3, \quad (6)$$

where H_1, H_2, and H_3 are components caused respectively by the turbulent and longitudinal diffusion and the resistance to mass transfer. According to the Giddings theory[13], H_1, H_2 and H_3 can be calculated from the equations

$$H_1 = 2\lambda d_p, \quad (7)$$

$$H_2 = \frac{2\tau D_m}{v}, \quad (8)$$

$$H_3 = \frac{qrd_p^2 v}{D_s} + \frac{\omega d_p v}{D_m}, \quad (9)$$

where λ, τ, q, and ω are constants which depend on the structure of the filler as well as the form and size of the column, d_p the diameter of the filler particles v the linear rate of migration of the mobile phase, D_m the diffusion coefficient of the test substance in the mobile phase, D_s the diffusion coefficient of the test substance in the stationary phase, and r a quantity which depends on the relative rate of migration of the substance analysed and the mobile phase. As a rule, the spreading of the band of the test substance associated with longitudinal molecular diffusion is small under the conditions of the migration of the mobile phase usually employed in liquid chromatography. On the other hand, the variance of the peak due to turbulent diffusion and the resistance to mass transfer are evidently smaller, the smaller the diameter of the sorbent particles (d_p).

Thus, the direct approach to an increase of the detection limit consists in shortening the diffusion pathway of the molecules of the test substance into the sorbent particles, which can be achieved in two ways: (a) by decreasing the intrinsic size of the sorbent particles and (b) by limiting the thickness of the sorbent layer as a result of its deposition on the surface of other (inert and impermeable) particles. Both procedures are used in the modern techniques for the preparation of effective sorbents.

The development of the technology for the synthesis of polymerisation (based on styrene and divinylbenzene) fine-grain ion-exchange sorbents led to the formation of effective cation- and anion-exchange spherical microbead resins, which have been used successfully for the rapid analysis of nano- and pico-gram amounts of nucleosides and nucleotides[20,21]. For example, Fig. 1 illustrates the separation of a mixture of ribonucleosides obtained by Burtis[21] using a column with the VC-10 (×10) cation exchanger (Sondell Scientific Instruments, USA). Certain characteristics of the spherical microbead polymerisation ion-exchange sorbents used in high-pressure liquid chromatography are listed in Table 1. It is noteworthy that the use of sorbents with a very small particle diameter necessitates an appreciable increase of pressure in order to ensure the required rate of elution. This imposes in its turn a limitation on the employment of sorbents whose polymer matrix consists of a styrene–divinyl–benzene copolymer with a low (up to 7–8%) degree of cross linking. It has been shown[22] that the gel properties of such sorbents, manifested by their swelling, contraction, and compaction, as well as the decrease of their permeability, etc., give rise to virtually insurmountable technical difficulties under conditions of high-pressure chromatography.

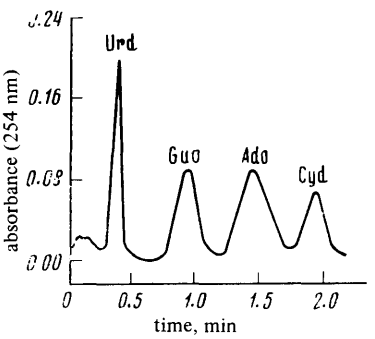


Figure 1. Separation of a mixture of ribonucleosides (300 nmoles) on a 2.4 mm × 25 cm column with a VC-10 (×10) cation exchanger in a 0.4 M $HCOONH_4$ solution (pH 4.75) at 55°C.[21]

Table 1. Certain characteristics of spherical microbead polymerisation sorbents.

Commercial name	d_p, μm	Functional groups	Capacity, mequiv. g^{-1}	Company
		Cation-exchange sorbents		
DC-X8	6—10	SO_3^-	5	Durrum Chemical Corp. USA
Aminex A-6	15—19	SO_3^-	5	Bio-Rad Laboratories, USA
Aminex A-7	7—11	SO_3^-	5	Ditto
VC-10 (×10)	7—14	SO_3^-	5	Sondell Scientific Instr.,USA
		Anion-exchange sorbents		
DA-X8	20	NR_4^+	4	Durrum Chemical Corp., USA
	6—10	NR_4^+	4	Ditto
Aminex A-27	12—15	NR_4^+	4	Bio-Rad Laboratories, USA
Aminex A-28	7—11	NR_4^+	4	Ditto

The possibility of decreasing the thickness of the sorbent bed, in which the molecules of the test substance diffuse, by converting into an ion exchanger only the surfaces of the carrier particles was first discussed in the

literature at an early stage by Pepper[23] and Weiss[24]. The successful practical utilisation of this idea in the separation of proteins on zeolite particles coated by a cation-exchange resin[25,26] stimulated the development of other surface ion-exchange sorbents and the study of their chromatographic properties[27,28]. Further development of methodological procedures involving the deposition of thin ion-exchange coatings onto glass, Teflon, and silica particles led to the creation of the so-called pellicular sorbents[29,30] and sorbents with a "controllable surface porosity".[31]

Certain characteristics of these sorbents, known under the commercial name of "Pellionex", are presented in Table 2. Sorbents of the "Pellionex" type are obtained by the copolymerisation of styrene and divinylbenzene on the surface of spherical glass particles with subsequent introduction of the appropriate functional groups[30]. In sorbents of the "Zipax" type the polymer containing functional groups is introduced into the pores of the particles[31]. Anion-exchange sorbents with a controllable surface porosity contain quaternary alkylammonium groups attached to a polyacrylic matrix and cation-exchange sorbents contain a sulphonated fluoro-polymer.

Table 2. Certain characteristics of pellicular ion-exchange sorbents and sorbents with a controllable surface porosity.

Commercial name	d_p, μm	Functional groups	Capacity, mequiv. g^{-1}	Company
Cation-exchange sorbents				
Pellionex SCX	40	SO_3^-	10	M.Reeve Angel and Co., USA
Zipax-SCX™	25—37	SO_3^-	3.2	Du Pont, Wilmington, Del., USA
Anion-exchange sorbent				
Pellionex SCX	40	NR_4^+	10	H.Reeve Angel and Co., USA
Zipax-SAX™	25—37	NR_4^+	12	Du Pont, Wilmington, Del., USA
Zipax-WAX™	25—37	NH_2	12	Ditto

The use of pellicular ion-exchangers and sorbents with a controllable surface porosity permits the rapid separation of complex mixtures of nucleotides as well as other structural components of the nucleic acid[9,32,33]. As an example, Fig. 2 presents the separation of a mixture of nucleoside mono-, di-, and tri-phosphates[29].

An undoubted advantage of surface ion-exchange sorbents is the possibility of using particles of greater size (up to 40–50 μm) in order to achieve the same efficiency of mixture separation as for fine (3–7 μm) polymerisation sorbents[9]. This permits their separation under the conditions of a high rate of elution and a considerably lower pressure. The low capacity of these sorbents[34] as well as the low mechanical strength of ion-exchange coatings, which sometimes leads to the breakdown of the surface layer during ordinary stirring of a suspension of the sorbent[9], must be regarded as their disadvantages. Furthermore, one should note the difficulty of preparing such sorbents and their high cost.

Systems with an inverted phase, known in the literature by the designations RPC-1–RPC-5,[35-38] can also be classified as surface ion-exchange sorbents. Some of them are used successfully at the present time for the separation of transport RNA[38] and the fractionation of oligo- and polynucleotides[39,40]. Silica gel or fluoro-polymer grains coated by a thin layer of liquid quaternary ammonium salts, such as trimethyloctyl- or trimethyldecyl-ammonium chlorides, are used as the stationary phase in these systems. The attainment of equilibrium between the liquid stationary and mobile phases during elution leads to a gradual "washing away" of the stationary phase. In order to increase the useful life of these sorbents, it is recommended that elution gradients and high flow rates are not used[41].

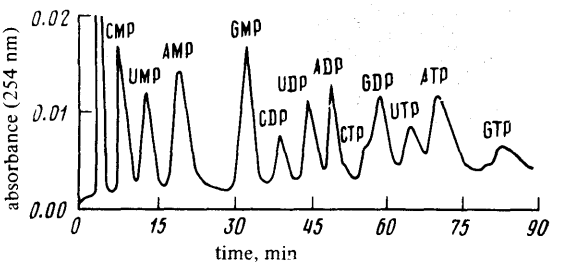


Figure 2. Separation of a mixture of nucleoside mono-, di-, and tri-phosphates (1.5–3.5 nmoles of each) on a 1 mm × 193 cm column with a Pellionex anion exchanger in a solution with a linear $HCOONH_4$ concentration gradient (0.04–1.5 M, pH 4.35) at 25°C. Rate of elution 12 ml h^{-1}; pressure 50 atm.[29]

Thus a general tendency in the development of modern high-pressure liquid chromatography is a change-over to sorbents ensuring a high rate of mass transfer and a high efficiency of the chromatographic process. A comparatively large number of effective ion-exchange sorbents, with a wide variety of structures and chromatographic properties, can be used in the analysis of the structural components of nucleic acids. The nature of the ion-exchange sorbent employed in many respects determines the conditions of the analysis. In the next section we shall consider in detail the methodological characteristics of the separation of mixtures of the most important structural components of nucleic acids under the conditions of high-pressure chromatography.

III. THE SEPARATION OF THE STRUCTURAL COMPONENTS OF NUCLEIC ACIDS BY HIGH-PRESSURE LIQUID CHROMATOGRAPHY

1. Analysis of the Heterocyclic Bases

The presence in the molecules of purine and pyrimidine bases of at least one and in most cases of several functional groups capable of acid or basic dissociation permits their conversion, depending on the acidity of the medium, into anions or cations and their separation by ion-exchange chromatography. Under the conditions of high-pressure column liquid chromatography, cation-exchange sorbents are most often used for the separation of the heterocyclic bases[30,42,43], although these compounds can also be separated with the aid of anion exchangers[44].

Table 3. Conditions for the separation of the heterocyclic bases by cation-exchange chromatography on pellicular sorbents and sorbents with a controllable surface porosity.

Compn. of mixture to be separated*	Type of sorbent	Column dimensions	Eluent composition	Rate of elution, ml h^{-1}	Pressure, atm	Elution temp., °C	Separation time, min	Refs.
Ura, Gua, Ade, Cyt	Pellionex SCX	1 mm × 300.7 cm	0.02 M $NH_4H_2PO_4$ (pH 5,50)	33,4	180	68	6	30
Ura (Thy), Gua, Cyt, Ade	Pellionex SCX	1 mm × 300 cm	0.05 M $NH_4H_2PO_4$ (pH 2,55)	40	115—143	70	10	42
Ura, Gua, Cyt, Ade	Pellionex SCX	1 mm × 250 cm	0.025 M $NH_4H_2PO_4$ (pH 4,40)	36	200	70	5	42
Ura, Hyp, Gua, Cyt, Ade, 6-MePu	Zipax-SCX™	2.1 mm × 100 cm	0.1 *N* HNO_3	120	53	63	15	43

*The compounds are quoted in order of increasing retention time on the column. The following abbreviations are used: Ura = uranil; Gua = guanine; Ade = adenine; Cyt = cytosine; Thy = thymine; Hyp = hypoxanthine; 6-MePu = 6-methylpurine.

It has been shown[30,42,43] that the effective separation of standard mixtures of heterocyclic bases can be achieved after 5–10 min using sorbents of the Pellionex or Zipax-SCX™ type. The detailed conditions for the separation of mixtures of heterocyclic bases are presented in Table 3.

In view of the comparatively small differences between the positive charges of the heterocyclic bases, they are usually separated under isocratic† elution conditions. The most satisfactory separation of the four nucleic acid bases on columns with a cation exchanger of the Pellionex type is achieved on elution with a 0.02 M $NH_4H_2PO_4$ solution (pH 5,2–5,5) at 68°C[30] (Fig. 3).

The behaviour of compounds in the course of chromatographic analysis is known to be determined both by the charge of their molecules and by their non-ionic affinity for the sorbent. Analysis of the elution sequence of the heterocyclic bases when the latter are separated on columns with sorbents of the Pellionex and "Zipax-SCX™" type (Table 3) permits the conclusion that ionic interactions are in this instance expressed more strongly than in the case where the usual polymerisation cation-exchange sorbents of the type Dowex-50, Amberlite IRC-50, etc. are used[45]. Indeed, when the eluent is a buffer at pH 5.5, the elution sequence of Uracil, guanine, (pK'_a = 3,3), adenine (pK'_a = 4,2), and cytosine (pK'_a = 4,6) corresponds to an increase of the pK_a values for the bases (i.e. to an increase of the positive charge of the molecules[46]). On the other hand, at lower pH values the order in which adenine and cytosine are eluted is reversed[42,43]. The data obtained by Horvath and Lipsky[30] also indicate an anomalous behaviour of guanine on columns with a Pellionex cation exchanger at pH 5.2 ("twinning" of the peak corresponding to guanine was observed).

It is apparently impossible to explain these phenomena from the standpoint of the non-polar interactions of the molecules of the test substance with the sorbent particles, because the non-polar affinity is almost independent of the pH of the medium[45]. The authors' suggestion that the anomalous behaviour of the test compounds on pellicular sorbents may be associated with kinetic effects in the course of the attainment of the sorption–desorption equilibrium involving the molecules of the test substance in the stationary and mobile phases also appears unconvincing[30].

†Isocratic elution is elution with a solution at a constant ionic strength.

It is noteworthy that the use of the Zipax-SCV™ cation-exchange sorbent with a controllable surface porosity permits the elution of bases with a solution having a lower ionic strength (even at a lower pH of the eluent), because of its lower capacity (Table 2).[43]

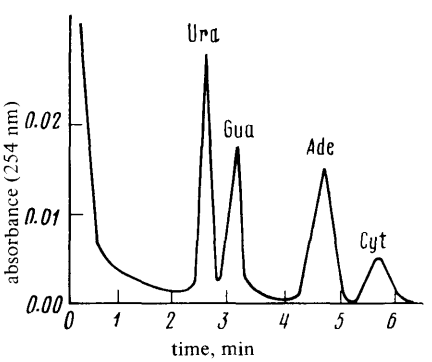


Figure 3. Separation of a mixture of heterocyclic bases (0.8 nmole of each) on a 1 mm × 300.7 cm column with a Pellionex cation exchanger in a 0.02 M $NH_3H_2PO_4$ solution (pH 5.5) at 68°C. Rate of elution 33.4 ml h^{-1}; pressure 177 atm.[30]

The possibility of employing spherical microbead polarisation cation-exchange resins under the conditions of high-pressure chromatography for the analysis of the heterocyclic bases was first demonstrated[47] in the determination of the amount of DNA in various tissues on the basis of their thymine context. The separation of the mixture of the heterocyclic bases formed as a result of the active hydrolysis of DNA has been achieved[48] on a column with the Aminex A-7 sorbent in 1 M NaH_2PO_4 (pH 3,4). Under these conditions, the non-ionic interactions of the mixture components with the organic matrix of the sorbent were suppressed by the increased elution temperature and the addition of alcohol to the solution. The necessity for the separation of mixtures of the heterocyclic bases arises fairly frequently in the course of a whole series of biochemical studies, particularly in the determination of the composition of RNA and DNA, in the elucidation of the

possible reaction pathways of free nucleotides *in vivo*, in the study of the mechanism of the action of certain enzymes etc., and in all cases high-pressure ion-exchange chromatography is as a rule one of the most effective analytical methods[8,9,49,50].

2. Analysis of Nucleosides

Numerous studies have been devoted to the separation and analysis of mixtures of nucleosides and their derivatives under the conditions of high-pressure ion-exchange chromatography[9,21,30,42]. This is associated primarily with the increased availability of highly purified enzymes in recent years, which permits the hydrolysis under mild conditions of ribo- and deoxyribo-nucleotide chains to nucleosides, as a result of which many problems involved in the study of the structures of nucleic acids can be solved at the level of the analysis of the nucleosides.

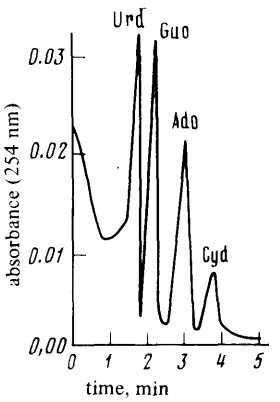


Figure 4. Separation of a mixture of nucleosides (approximately 0.3 of a nmole of each) on a 1 mm × 151.7 cm column with a Pellionex cation exchanger in a 0.02 M $NH_4H_2PO_4$ solution (pH 5.5) at 24°C. Rate of elution 32.5 ml h^{-1}; pressure 38 atm.[22]

Table 4 summarises the literature data for different types of sorbents and separation conditions most frequently used in the analysis of nucleosides. Evidently both spherical microbead polymerisation cation-exchange resins[21] and pellicular cation exchangers of the Pellionex[22,41] type as well as Zipax-SCX™ sorbents with a controlled surface porosity[9] can be used for the separation of nucleosides and many of their derivatives under the conditions of high-pressure liquid chromatography. However, a more detailed analysis of the results of the separation obtained using the above sorbents suggests that preference should be given to spherical microbead polymerisation resins, because the sorption of uridine and thymidine on columns with sorbents of the Pellionex and Zipax-SCX™ types under the conditions of optimum separation of the nucleoside peaks is extremely low, as noted by Horvath[9]. Because of this, the above nucleosides are eluted in a very narrow band and their peaks are as a rule superimposed on the "injection peak", which normally accompanies the introduction of the analysed solution into the column (Fig. 4). This hinders and sometimes altogether precludes a correct interpretation of the results of the separation process. On the other hand, the use of spherical microbead cation-exchange resins, whose polymeric matrix in all probability ensures a fairly intense sorption, makes it possible to overcome these difficulties. The best results in the separation of nucleosides and many of their derivatives were obtained by Burtis[21] on columns with the finest DC-x8 (Fig. 1) and VC-10 cation-exchange resins. Burtis also confirmed the theoretical conclusion that the maximum efficiency of the separation can be achieved when the column is filled with finer particles (Table 5).

Table 5. The efficiency of columns with spherical microbead cation-exchange polymerisation sorbents in the separation of nucleosides in 0.4 M ammonium formate solution (pH 4.55).[42]

Sorbent	d_p, μm	Column dimensions	Temp., °C	Rate of elution		Pressure, atm	N	H, mm
				ml h^{-1}	cm s^{-1}			
DC-×8	3—7	2.4 mm × 25 cm	55	40	0.61	326	1042	0.24
Aminex A-7	7—10	2.4 mm × 25 cm	55	35	0.54	300	806	0.31
VC-10 (×10)	7—14	2.4 mm × 25 cm	85	85	1.30	334	338	0.74

Table 4. Conditions for the separation of nucleosides by high-pressure cation-exchange chromatography.

Composition of the mixture to be separated*	Type of sorbent	Column dimensions	Eluent composition	Rate of elution, ml h^{-1}	Pressure, atm	Elution temp., °C	Separation time, min	Refs.
Urd, Guo, Ado, Cyd	Pellionex SCX	1 mm × 151.7 cm	0.02 M $NH_4H_2PO_4$ (pH 5.60)	25.5	140	39	4	30
dThd, dGuo, dAdo, dCyd	Aminex A-7	2.4 mm × 25 cm	2.4 M $HCOONH_4$ (pH 4.55)	10	70	55	20	42
Urd, Guo, Ado, Cyd	Pellionex SCX	1 mm × 300 cm	0.012 M $NH_4H_2PO_4$ (pH 3.50)	33	150—170	50	16	42
Urd, Ino, Guo, Ado, Cyd	DC-×8	2.4 mm × 25 cm	0.4 M $HCOONH_4$ (pH 4.75)	40	340	55	4	9
Urd, Guo, Ado, Cyd	VC-10 (×10) (17-14 μm)	2.4 mm × 24 cm	0.4 M $HCOONH_4$ (pH 4.50)	50	215	75	7	21
Urd, Guo, Ado, Cyd	VC-10 (×10) (7-10 μm)	2.4 mm × 25 cm	0.4 M $HCOONH_4$ (pH 4.50)	50	330	75	4	21

*The compounds are quoted in order of increasing retention time on the column. The following abbreviations are used: Urd = uridine; dAdo = deoxyadenosine; dGuo = deoxyguanosine; dThd = deoxythymidine; dCyd = deoxycytidine; Ino = inosine.

Spherical microbead polymerisation cation-exchange sorbents have been used successfully in the analysis of the enzymatic hydrolysates of many RNA specimens in order to elucidate their nucleoside composition[9,21,42] and also for the investigation of the content of various minor nucleosides in DNA[51] and individual transport RNA[34,50] preparations.

Mixtures containing simultaneously ribo- and deoxyribo-nucleosides can be separated comparatively rapidly on columns with the Aminex A-7 sorbent proposed by Duch and Laskowski[52]. The difference between the retention times of ribose and deoxyribose derivatives can be most probably accounted for by the secondary interactions of the nucleosides with the sorbents (by hydrogen bonding, etc.) rather than ionic interactions. The method has been used successfully to determine the impurity amounts (down to 0.2–0.4%) of RNA in DNA preparations after the enzymatic degradation of the polymeric molecules to nucleosides[52].

The traditional procedure for the preparation of carbohydrate-borate complexes, proposed as early as 1951[53] and developed in detail subsequently[45,54], has also been used successfully to separate ribo- and deoxyribo-nucleosides under the conditions of effective liquid chromatography. By combining ion-exclusion and partition chromatography in columns with the Aminex-A-6 sorbent using a 0.1 M ammonium borate solution as the eluent (pH 7.4), it is possible to separate ribo- and deoxyribo-nucleosides in view of the capacity of the former for complex formation with the borate ions of the eluent. The ribose derivatives converted into anions under these conditions are "expelled" from the negatively charged stationary phase.

Ion-exclusion chromatography has been used recently on an increasing scale for the separation of mixtures of nucleosides. The principle of this method has been frequently discussed in the literature[55,56]. The difference between the negative charges of the molecules as well as the different degrees of their non-specific sorption permit a comparatively rapid separation in an alkaline medium (pH 9.5) of complex mixtures of nucleosides on columns with Aminex A-6 cation-exchange resins[57,58].

The use of finer polymerisation resins and higher flow rates in ion-exclusion chromatography apparently makes it possible to increase greatly the efficiency of the method, which thus leads to considerable prospects for the employment of the high-pressure chromatographic technique.

3. Analysis of Mononucleotides and Their Derivatives

Anion-exchange sorbents are usually employed for the separation of mixtures of mononucleotides, because these compounds and the majority of their derivatives exist in the anionic form as a result of the acid dissociation of the phosphate groups ($pK_a^1 = 1$; $pK_a^2 = 6-7$[59]) over the entire range of the pH of the eluents normally used in ion-exchange chromatography. The data presented in Table 6 show that the Pellionex anion exchangers and the Zipax-SAX^{TM} sorbents are used most extensively for the analysis of these compounds under the conditions of high-pressure chromatography. The employment for these purposes of columns with spherical microbead polymerisation anion-exchange resins is limited[60,61], which in our view is due to the breakdown of the column packing in consequence of

Table 6. Conditions for the separation of nucleotides and their derivatives by high-pressure anion-exchange chromatography.

Compn. of mixture to be separated*	Type of sorbent	Column dimensions	Eluent compn.	Rate of elution, ml h^{-1}	Elution temp., °C	Pressure, atm	Separation time	Refs.
P-2′-Cyd, P-3′-Cyd, P-2′-Urd, P-3′-Urd, P-2′-Ado, P-3′-Ado, P-2′-Guo, P-3′-Guo	Dowex-1 × 8 (~ 10 μm)	0.25 mm × 75 cm	(0.05—1.0 *M*) CH_3COONa (pH 4.40) **	60	45	285	240	60
AMP, ADP, ATP	Pellionex	1 mm × 300 cm	0.75 *M* KH_2PO_4 (pH 4.2) **	55	80	186—214	4	42
CMP, UMP, AMP, GMP, CDP, UDP, ADP, GDP, CTP, UTP, ATP, CTP	Pellionex	1 mm × 193 cm	(0.04—1.5 *M*) $HCOONH_4$ (pH 4.35) **	12	25	54	90	30
CMP, UMP, AMP, IMP, GMP, XMP	Pellionex	1 mm × 300 cm	0.01 *M* KH_2PO_4 (pH 3.25)—1 *M* KH_2PO_4 (pH 4.20) **	15	70	200	55	42
dCMP, dTMP, dAMP, dGMP	Pellionex	1 mm × 300 cm	0.01 *M* KH_2PO_4 (pH 3.25)—1 *M* KH_2PO_4 (pH 4.20) **	57	80	170—200	10	42
P-2′-Cyd, P-3′-Cyd, P-2′-Urd, P-3′-Urd P-2′-Ado, P-3′-Ado, P-2′-Guo, P-3′-Guo	Pellionex	1 mm × 300 cm	0.01 *M* KH_2PO_4 (pH 3.35)—1 *M* KH_2PO_4 (pH 4.20) **	48	75	207	30	9
CMP, UMP, AMP, GMP	Zipax-SAX^{TM}	2.1 mm × 100 cm	0.006 *M* H_3PO_4, 0.002 *M* KH_2PO_4 (pH 3.75) ***	114.6	60	64	7	43
dCMP, dTMP, dAMP, dGMP	Zipax-SAX^{TM}	1 mm × 100 cm	0.008 *M* KH_2PO_4 (pH 4.40) ***	2.5	20	150	70	62

*The compounds are quoted in order of increasing retention times on the column. The following abbreviations are used: P-2′(3′)-Cyd = cytididine 2′(3′)-phosphate; P-2′(3′)-Urd = uridine 2′(3′)-phosphate; P-2′(3′)-Ado = adenosine 2′(3′)-phosphate; P-2′(3′)-Guo = guanosine 2′(3′)-phosphate; dCMP = deoxyribocytidine 5′-phosphate; dTMP = deoxyribothymidine 5′-phosphate; UMP = uridine 5′-phosphate; dAMP = deoxyriboadenosine 5′-phosphate; dGMP = deoxyriboguanosine 5′-phosphate; IMP = inosine 5′-phosphate; XMP = xanthosine 5′-phosphate.

**Gradient elution.

***Isocratic elution.

the change in the swelling of the sorbent. In addition, a change in the composition of the eluting buffer normally leads to the compaction of the polymerisation sorbents, which is extremely undesirable under the conditions of high-pressure chromatography.

Attention should be drawn to the difference between the conditions for the separation of mixtures of nucleotides on various sorbents (Table 6), which may be caused by the different chemical structures of the sorbents themselves. Thus the separation of certain mixtures (for example of ribonucleotides, deoxyribonucleotides, etc.) under the conditions of isocratic elution[43,62] can be achieved on columns with the Zipax-SAX^{TM} ion exchanger. In particular, an effective and rapid separation of nucleoside 5′-phosphates has been achieved on columns with this sorbent using a 0.002 M KH_2PO_4 solution at pH 3.75 (Fig. 5). The use of a Pellionex carrier for this purpose requires the application of gradient elution[9,42]. Changes in the pH of the eluent are also frequently used together with changes in concentration in order to improve the resolution and shape of the peaks[9,42,43].

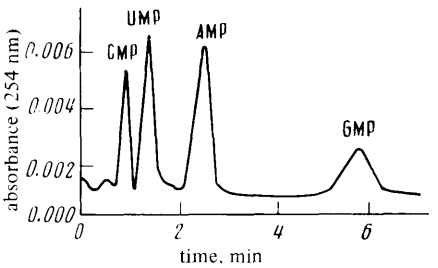


Figure 5. Separation of a mixture of nucleoside 5′-phosphates on a 2.1 mm × 100 cm column with the Zipax SAX^{TM} sorbent in a 0.002 M KH_2PO_4 solution (pH 3.75) at 60°C. Rate of elution 114.6 ml h^{-1}; pressure 64 atm.[43]

The position of the phosphate group in the nucleotide molecule influences the degree of protonation of the heterocyclic base[59] and hence the overall charge of the molecule and permits thereby the separation of isomeric nucleoside phosphates[9]. The conditions indicated in Fig. 6 for the separation of a mixture of nucleoside 2′,3′-phosphates have been used to analyse alkaline hydrolysates of RNA.[53]

The technique of high-pressure anion-exchange chromatography and the use of effective sorbents permit comparatively rapid separation of mono-, di-, and triphosphates of ribo- and deoxyribo-nucleosides[9,29,54] (see also Fig. 7), which require elution for many hours under the conditions of the usual chromatography[65]. Table 7 presents the retention times of nucleoside mono-, di-, and triphosphates as well as a number of their derivatives obtained by Brown[66] in chromatography on a Pellionex anion exchanger, which are extremely useful for the interpretation of chromatograms obtained in the separation of mixtures of free nucleotides and their derivatives from various extracts.

The possibility of rapid analysis of picomolar amounts of adenosine 5′-phosphate, adenosine 3,5′-cyclic phosphate, and adenosine 5′-triphosphate on columns with a Pellionex anion exchanger has been studied by a number of investigators in order to determine the activities of adenylate cyclase and adenosine 3′,5′-cyclic phosphate diesterase, which catalyse the reactions of the corresponding adenylic acid derivatives in tissue cells[67-69].

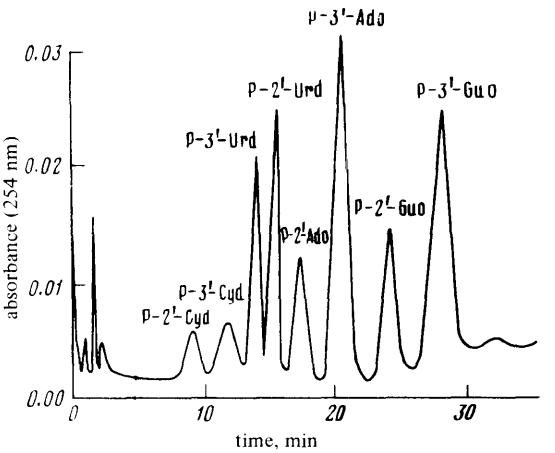


Figure 6. Separation of a mixture of nucleoside 2′,3′-phosphates (approximately 1 nmole of each) on a 1 mm × 300 cm column with a Pellionex anion exchanger in a solution with a linear KH_2PO_4 concentration gradient (0.01 M, pH 3.35–1.0 M, pH 4.20) at 75°C. Rate of elution 48 ml h^{-1}; pressure 207 atm.[64]

Table 7. The retention times of nucleotides and their derivatives in chromatography on a 1 mm × 300 cm column with a Pellionex anion exchanger*.

Compound**	Time, min	Compound**	Time, min	Compound**	Time, min
CMP	10	NAD+	8.5	CTP	46
UMP	12	UDP-Glc	24	UTP	49.5
TMP	14	CDP	29	TTP	54
IMP	18	UDP	31	ATP	60
AMP	19	TDP	33	GTP	65
GMP	23	ADP	38		
6Me-sPuoMP	27	NADH	39		
sGMP	32	GDP	43		
XMP	34	UDP-GlcCOOH	44		

* Chromatographic conditions[66]: elution in a linear phosphate buffer gradient [0.015 M KH_2PO_4 (pH 3.25)–0.25 mm KH_2PO_4 (pH 4.20), 2.2 M KCl] at 75°C. Rate of elution 12 ml h^{-1}.

** The following abbreviations are used: 6Me–sPuoMP = 6-methylthioribosylpurine 5′-phosphate; sGMP = mercaptoguanosine 5′-phosphate; NAD^+, NADH = nicotinamide-adenine dinucleotide (oxidised and reduced); UDP-Glc = uridine diphosphate-glucose; UDP-GlcCOOH = uridine phosphate-glucuronic acid.

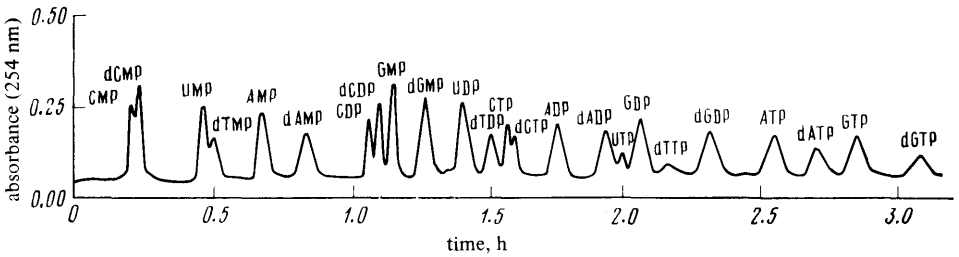


Figure 7. Separation of a mixture of ribo- and deoxyribo-nucleoside phosphates on a 0.62 mm × 20 cm column with the Aminex A-28 sorbent in a solution with a sodium nitrate concentration gradient (pH 8.6) at 70°C. Rate of elution 36 ml h^{-1}; pressure 15 atm.[64]

The successful separation of a mixture of nucleosides and nucleotides on columns with the Aminex A 28 polymerisation anion exchanger[48] (Fig. 8) permits rapid analysis of the oligonucleotide end groups, which is one of the essential stages in the study of the primary structure of the fragments of native nucleic acids.

Numerous studies on the content of the mononucleotides and their derivatives in various extracts in connection with biochemical and medicobiological research[70-73] also indicate the unique possibilities of high-pressure liquid chromatography, with which none of the available analytical methods can compete nowadays in this field.

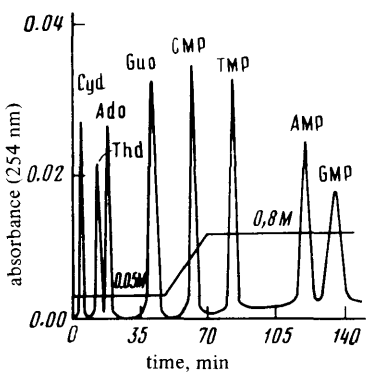


Figure 8. Separation of a mixture of deoxyribonucleosides and deoxyribonucleoside 5′-phosphates on a 1.8 mm × 50 cm column with the Aminex A-28 sorbent in a solution with a concentration gradient of a phosphate–borate buffer (0.05–0.8 M, pH 7.8) at 60°C. Rate of elution 25 ml h^{-1}; pressure 220 atm.[48]

4. Chromatography of Oligo- and Poly-nucleotides

Highly efficient separation of oligo- and poly-nucleotides with respect to both chain length and nucleotide composition is one of the urgent problems in the analytical chemistry of nucleic acids. The possibilities of high-pressure liquid chromatography as regards the solution of this problem have so far been inadequately investigated. The choice of sorbents for the separation of oligo- and poly-nucleotides whose behaviour in chromatography is determined not only by the structure of heterocyclic bases, the nature of the sugar residues, and the overall charge of the molecule but also by the molecular weight and characteristics of the steric interaction with the surface of the ion exchanger[77,78], constitutes a fairly complex problem. In this connection the permeability of sorbent particles to large molecules assumes particular importance. Thus the spherical microbead polymerisation anion exchangers with a high content of cross-links (up to 8–10%), used in high-pressure liquid chromatography are either altogether impermeable to polyanions with a high molecular weight or their permeability is extremely low owing to the low rate of diffusion of these compounds into the sorbent particles. On the other hand, as mentioned above, sorbents with a smaller content of cross-links are not used in high-pressure liquid chromatography in view of their more pronounced gel properties. They can be employed only as an ion-exchange film coating in the so-called pellicular sorbents[9]. However, the possibility of using such sorbents in the practical chromatography of oligonucleotides has been scarcely elucidated. Pellicular anion exchangers have so far been used only for the separation of dinucleotides[9,42,64].

The RPC-3 and RPC-5 anion-exchange systems with an inverted phase are used most frequently for the analysis of oligo- and poly-nucleotides[35-38]. These sorbents, first introduced into liquid chromatography by Kelmers and coworkers[35] for the fractionation of transfer RNA, are nowadays used successfully also for the separation of oligo- and poly-nucleotides[39,40]. Their chromatographic characteristics depend on the chemical nature of the liquid stationary phase, which usually consists of liquid tetraalkylammonium salts, as well as the structure of the particles which serve as the solid support.

The solid supports in the RPC-3 and RPC-4 systems consist of silica or silica gel particles. To ensure the firm binding of the liquid quaternised amine to the surface of such particles, the latter are silylated, i.e. treated with trialkyl- or triarylchlorosilanes[37,39]. The data obtained by Holton et al.[39] suggest that the use of chlorotriphenylsilane for this purpose is preferable, because it improves considerably the chromatographic properties of the sorbent. Holton et al.[39] were able to achieve with the aid of the sorbents the separation of thymidylic acid oligonucleotides under the conditions of isocratic elution with a 0.5 M solution of an ammonia–formate buffer (pH 5.25). The RPC-5 system, where fluoro-polymer particles are used as the solid support, also proved to be effective for the

fractionation of oligo- and poly-nucleotides with respect to their chain length[40]. Use of the system enabled the authors[40] to achieve the separation of a 60-component mixture of homologous nucleotides having the general formula $(Ap)_xU$ ($x = 1, 2, 3, \ldots$).

The lack of information concerning the separation on these sorbents of mixtures of oligo- and poly-nucleotides with a more complex structure precludes so far an assessment of the prospects and limits of their employment. There is no doubt that the capacity of certain oligonucleotides for self aggregation in aqueous salt solutions[79] and the associated enhancement of the role of secondary non-ionic interaction create certain difficulties in their chromatography on sorbents of this kind. On the other kind, the impossibility of employing under the conditions of high-pressure liquid–liquid chromatography of organic compounds such as urea, dioxan, etc. (normally used to suppress secondary interactions of this kind[80,81]), owing to the considerable increase of the viscosity of the mobile phase and the increase of the solubility in the latter of the liquid stationary phase, aggravate these difficulties still further.

In this connection the study of the possibility of using for the separation of mixtures of oligo- and poly-nucleotides of coarsely porous sorbents with a bound ion-exchange phase[41] in which the hydrocarbon groups of amines are attached to silica gel particles via strong covalent bonds, which have become available in recent years, appears to be very promising. These sorbents include Partisil-10 SAX (Whatman, England) and Lichrosorb NH_3 (E.Merk, German Federal Republic). While possessing all the advantages of systems with an inverted phase, they permit an extensive variation of the composition of the eluates, extending thereby appreciably the scope of their applications.

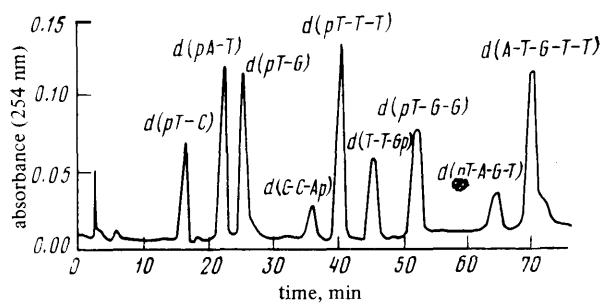


Figure 9. Chromatography of oligodeoxyribonucleotides on a 2 mm × 25 cm column filled with silica gel (particle size approximately 10 μm) with covalently attached hydrocarbon groups of primary amines in a solution with a linear phosphate buffer concentration gradient (0.10 M KH_2PO_4, pH 3.30–0.75 M KH_2PO_4, pH 4.25) at room temperature. Rate of elution 60 ml h^{-1}; pressure 180 atm.[81]

Data obtained by Aukati et al.[81] have shown that columns containing silica gel with grafted aminoalkyl groups can be used successfully for the fractionation of olinucleotides with respect to both their length and composition (Fig. 9). The stability of the stationary phase in such columns with respect to organic solvents and their stability over a wide pH range (1–8.5) ensure a satisfactory reproducibility of the analytical results and a long lifetime of the columns[82].

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Summarising the data discussed in this review, one must conclude that the application of modern high-pressure ion-exchange chromatography permits the successful separation of ultramicroanalytical amounts of a very great variety (as regards complexity) of mixtures of the structural components of nucleic acids. The commercial availability of the necessary chromatographic apparatus and ion-exchange sorbents ensuring a high rate of mass transfer and the associated efficiency of the chromatographic process permit the employment of the high-pressure liquid chromatographic technique in the solution of a very large number of problems in research on the composition, structure, and functional role of nucleic acids. One may hope that further investigation of the possibilities of the sorbents already available and the appearance of new ion-exchange materials will eventually permit a further extension of the limits of applicability of the high-pressure liquid–liquid chromatographic technique, whose efficiency is in many instances comparable to that of gas chromatography.

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The Oxygen Radical-anion O_2^- in Chemical and Biochemical Processes

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The review considers studies of the chemical and biochemical processes with participation of the oxygen radical-anion O_2^- and its principal physicochemical characteristics. Methods for the preparation of O_2^- in aqueous and aprotic media, are examined as are protonation, nucleophilic substitution and oxidation-reduction reactions involving this species, the formation of O_2^- in enzymatic processes and in photosynthesis, the role of O_2^- in the oxygenation of haems, phagocytosis, pathological processes, the toxic effect of oxygen etc.
The bibliography includes 675 references.

CONTENTS

I.	Introduction	527
II.	Physical properties of O_2^-	528
III.	Chemical properties of O_2^-	528
IV.	The formation of O_2^- and its interaction with biologically active substrates	531
V.	The participation of O_2^- in enzymatic oxidation-reduction processes	533
VI.	The participation of O_2^- in the oxidation-reduction reactions of natural macrocyclic metal complexes and their models	536
VII.	The toxic effect of O_2^- and its involvement in pathological processes and phagocytosis	537

I. INTRODUCTION

In 1957-1960 Emanuel' and coworkers[1-3] demonstrated for the first time the importance of the involvement of free radicals in normal and pathological vital processes of organisms. One of the most convincing confirmations of the free-radical hypothesis in biology proved to be the identification in biological systems of the oxygen radical-anion O_2^-. The hypothesis of the involvement of O_2^- in enzymatic processes was put forward by Fridovich and Handler in 1958-1962[4-6]. However, as early as 1934 the possible involvement of O_2^- in chemical reactions was pointed out by Haber and Weiss[7,8] in a study of the decomposition of hydrogen peroxide and the oxidation of metal ions by oxygen in aqueous solutions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^- , \quad (1)$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HOO^{\cdot} , \quad (2)$$

$$HOO^{\cdot} \rightleftarrows H^+ + O_2^{\cdot-} , \quad (3)$$

$$Fe^{2+} + O_2 \rightleftarrows Fe^{3+} + O_2^{\cdot-} . \quad (4)$$

At the present time the formation of O_2^- has been demonstrated in many chemical reactions. Studies on biochemical processes involving O_2^- (enzymatic reactions

catalysed by oxidoreductases, the interaction of haems with oxygen, the mechanism of the protection of the organism from the toxic effect of oxygen, problems of phagocytosis, etc.) have begun to develop, particularly vigorously. A number of reviews devoted to various problems of the chemistry and biochemistry of O_2^- have been published recently[9-19]. In the present review we thought it useful to survey all the principal investigations of the chemical and biochemical properties of O_2^-.

II. PHYSICAL PROPERTIES OF O_2^-

In the "free" oxygen radical-anion the unpaired electron is delocalised over both oxygen atoms. However, in liquid and solid phases there is a possibility of the formation of ion pairs of O_2^- and counterions—metal or organic cations. The compounds NaO_2 and KO_2 are crystalline substances which are sparingly soluble in organic solvents. In contrast to them, NR_4O_2 (R = alkyl) readily dissolves in dimethylformamide (DMF), dimethyl sulphoxide (DMSO), acetonitrile, etc. The structure of MO_2 (M = metal) was investigated by infrared and Raman spectroscopy[20-24] and EPR[25-34]. The EPR spectrum of O_2^- has been observed only at a low temperature (77 K). It was found[25] that the EPR spectrum of O_2^-, obtained by the electrochemical reduction of oxygen in DMF, is characterised by an anisotropic g-factor ($g_1 = 2.006$, $g_2 = 2.009$, and $g_3 = 2.041$). Analogous EPR spectra were obtained when O_2 was reduced in pyridine[26], for MO_2 complexes (M = Ti^{4+}, Hf^{4+}, Tl^{4+}, Sn^{4+}, etc.) in solution[30,31], and for crystalline NaO_2.[29] In addition, using a rapid freezing technique, the EPR spectra of O_2^- and $^{17}O_2^-$ have been obtained[27,28] in the course of the oxidation of xanthene by xanthene oxidase. The observed values of the g-factor can be accounted for by the interaction of O_2^- with the solvent or cations[34]. Apart from the complexes of O_2^- with metal cations, its compounds with cobalt(III)[35-37] and rhodium(III)[38] complexes, which can exist both as monomers and dimers, have been described.

It has been found by the technique of pulse radiolysis that the ultraviolet spectrum of O_2^- in aqueous solutions has a maximum at 250 nm (ϵ = 1800–2000 litre mole^{-1} cm^{-1}).[39-44] λ_{max} = 462 nm for O_2^- in solution in pyridine[45]. The spectrum of O_2^- in acetonitrile, with a maximum at 250 or 255 nm, has been described[46,47]. However, the observation of this maximum may be a consequence of instrumental errors[47], particularly since it is known[48,49] that the absorption maxima of radical-anions in aprotic solvents should be displaced towards longer wavelengths compared with aqueous solutions in consequence of the hydration of the radical-anions in the latter.

The reduction of oxygen in aprotic solvents involves a one-electron mechanism. It has been shown[25] that O_2 is reduced in DMSO and DMF at $E_{1/2}$ = −0.73 and −0.80 V respectively and O_2^- is reduced at −2.40 and −2.8 V. Analogous data were obtained for the reduction of O_2 in DMSO on platinum, gold, and mercury[26,50,51] and in pyridine, dimethylacetamide (DMA), acetonitrile, acetone, methylene chloride, etc. on mercury[26,52-54]. The one-electron reduction of oxygen is quasi-reversible[26], the deviation from reversibility being apparently due to the protonation and dismutation of O_2^-.[55] Owing to the rapid reaction of O_2^{2-} with the solvent, the reduction of O_2^- is fully irreversible[56]. When oxygen is reduced in DMF and DMSO in the presence of metal cations, there is an anodic shift of the one-electron wave (owing to the formation of MO_2 ion pairs) and a mixture of the corresponding metal peroxides and superoxides is formed[51,57].

In contrast to aprotic solvents, in aqueous solutions oxygen is reduced electrochemically via a formally two-electron mechanism consisting of two one-electron stages[58]

$$O_2 \xrightarrow{e} O_2^{\cdot-} \xrightarrow{H^+} HOO^{\cdot} \xrightarrow{e} HOO^- . \qquad (5)$$

However, it has been observed recently[59,60] that, in the presence of surface-active substances (quinoline or triphenylphosphine oxide) the protonation of O_2^- on the surface of the cathode is difficult. Under these conditions and at high pH (when the rate of disproportionation of O_2^- is low), O_2^- can be obtained also in aqueous solutions. It has also been suggested that O_2^- be generated by the continuous radiolysis of a formate solution saturated with oxygen[50,51].

Recently much attention has been devoted to a more accurate determination of the O_2 reduction potential in aqueous solution—a parameter which is of great biochemical importance. The initial value $E_0(O_2/O_2^-) = -0.56$ V (relative to the hydrogen electrode)[63] is undoubtedly too low. Thermodynamic calculation yielded $E_0(O_2/O_2^-) = -0.18$ V.[44] Wood examined critically the published values of E_0[60,63,65,66] and concluded that $E_0 = -0.33 \pm 0.01$ V.[64] Then, in a later study[67], a higher value $E_0(O_2/O_2^-) = 0.07 \pm 0.02$ V was again obtained. However, this problem can now apparently be regarded as solved: in a number of independent studies on the reduction of O_2 in the presence of surface-active substances[68] and of the equilibria in the reactions of O_2^- with quinones[69-71] and with cytochrome c[72] values in the range $E_0(O_2/O_2^-) = -0.28$ to −0.32 V were obtained. One should bear in mind that these values were calculated for $p_{O_2} = 1$ atm; adjustment to $[O_2] = 1$ M leads to $E_0(O_2/O_2^-) = -0.11$ to −0.15 V respectively. The higher O_2 reduction potential in aqueous solutions compared with aprotic solvents can probably be accounted for by the difference between the O_2^- solvation energies[73]. Indeed the energy of solvation of O_2^- by water molecules in the gas phase is higher by 2–3 kcal mole^{-1} then the energy of solvation by acetonitrile molecules[74].

III. CHEMICAL PROPERTIES OF O_2^-

1. The Lifetime of O_2^- in Solution

Earlier it was postulated that the lifetime of O_2^- in aqueous solution is very short and that the disproportionation rate constant is high: $k_6 = 2 \times 10^7$ litre mole^{-1} s^{-1}:[75-77]

$$O_2^{\cdot-} + O_2^{\cdot-} \xrightarrow{2H_2O} H_2O_2 + O_2 + 2HO^- . \qquad (6)$$

However, it was later shown that $k_6 < 10$ litre mole^{-1} s^{-1},[42,68,78] so that at pH > 7 O_2^- exists for a relatively long time (the half-life is approximately 1 min at pH 13)[68]. According to the latest data, reaction (6) can be altogether neglected ($k_6 < 0.3$ litre mole^{-1} s^{-1}) and in real aqueous solutions O_2^- disappears as a result of reaction with HOO$^{\cdot}$ or impurities[79].

In aprotic solvents O_2^- exists much longer. Depending on the oxygen reduction conditions and primarily on the possibility of contact between O_2^- and aqueous solutions and the anolyte as well as the O_2^- concentration, the half-life of O_2^- in basic solvents (DMF, DMSO) is 1–20 h[50,73,80-84]. In acetonitrile the stability of O_2^- is much lower[84,85] and one cannot therefore agree with recommendations concerning the use of acetonitrile solutions of O_2^- in biochemical experiments[46,47]. Data[46] showing the instability of O_2^- in DMF can probably be accounted for by the presence of moisture and other impurities in the solvent employed[83].

2. The Reactions of $O_2^{\cdot-}$ in Aqueous Solutions

The oxygen radical-anion can be formed in aqueous solutions in various oxidation-reduction processes, for example in the Haber–Weiss cycle mentioned previously[7,8], and also in the oxidation of hydroquinones[86] and anthranols[87] in an alkaline medium. However, photolysis and radiolysis of oxygen-saturated aqueous solutions, which can contain hydrogen peroxide or formic acid, are nowadays widely used for the generation of $O_2^{\cdot-}$†:

$$H_2O \rightarrow H^{\cdot} + HO^{\cdot} + e(aq) \quad , \tag{7}$$

$$e(aq) + O_2 \rightarrow O_2^{\cdot-} \quad , \tag{8}$$

$$HO^{\cdot} + HCOO^- \rightarrow H_2O + COO^{\cdot-} \quad , \tag{9}$$

$$COO^{\cdot-} + O_2 \rightarrow CO_2 + O_2^{\cdot-} \quad , \tag{10}$$

$$H^{\cdot} + O_2 \rightarrow HOO^{\cdot} \tag{11}$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HOO^{\cdot} \tag{12}$$

$$HOO^{\cdot} \rightleftarrows H^+ + O_2^{\cdot-} \quad . \tag{13}$$

Table 1. The rate constants for the formation of $O_2^{\cdot-}$ by reaction (14) in aqueous solutions at 25°C.

A	pH	$10^9 k_{14}$, litre mole^{-1} s^{-1}	References
Benzoquinone*	7	$4.5 \cdot 10^{-5}$	72
2,5-Dimethylbenzoquinone	7	0.0048	71
Duroquinone	7	0.2±0.05	89
Duroquinone	7	0.22	70
Menadione	7	0.2	89
Menadione	7	0.24	70
Indigodisulphonate	7	0.03	70
Anthraquinone-1-sulphonate	—	0.42	90
Anthraquinone-2-sulphonate	—	0.46	90
Acetophenone	12	2.3	91
Adenine	—	3.6	91
Thymine	—	3.5	91
CO_2	6.9	4.6	92
CO_2	—	2.4	93
CO_2	—	4.2±0.4	94
Dimethyl fumarate	—	2.2	95
CH–CO, ‖ >NC$_2$H$_5$, CH–CO	—	2.0	96
Dithiothreitol	—	1.37	97
Nifuroxime	—	1.5	98
SO_2**	—	0.0013	99
Ru(bipy)$_3^{2+}$***	6—7	1.8	101
Ru(bipy)$_3^{2+}$***	6—7	7.2±0.8	102
Ru(bipy)$_3^{2+}$***	—	7.4	103
Pyrazine****	13.6	1.9	100
Quinoxaline****	13.6	0.37	100

*Method of competition kinetics.
**The stopped flow method.
***Flash photolysis; in the remaining cases pulse radiolysis was used to determine the constants.
****Neutral protonated radical.

In addition $O_2^{\cdot-}$ can also be formed in electron transfer processes:

$$A^{\cdot-} + O_2 \rightarrow A + O_2^{\cdot-} \quad . \tag{14}$$

†It has recently been suggested that KO_2 be used to investigate the reactions of $O_2^{\cdot-}$ in aqueous solutions[78,88]. However, the accuracy of quantitative calculations in this case is doubtful.

The rate constants for these reactions are listed in Table 1. The formation of $O_2^{\cdot-}$ in the oxidation by oxygen of macrocyclic nickel(I) complexes, on the one hand, and of univalent Ag^+, Cd^+, Co^+, $HgCl^+$, Pb^+, and Zn^+ ions, on the other, has been described by Tait et al.[104] and Sellers and Simic[105] respectively.

Neutral organic radicals as a rule react with oxygen to form peroxy-radicals. However, the final product of the oxidation of α-hydroxyalkyl radicals in an alkaline medium can be $O_2^{\cdot-}$:[106,107]

$$HOCR_2OO^{\cdot} \overset{pH\ 9.8}{\rightleftarrows} H^+ + {}^-OCR_2OO^{\cdot} \rightarrow O_2^{\cdot-} + CR_2O \quad . \tag{15}$$

A bimolecular process is also possible:

$$HO^- + HOCR_2OO^{\cdot} \rightarrow H_2O + {}^-OCR_2OO^{\cdot} \rightarrow O_2^{\cdot-} + CR_2O \quad . \tag{16}$$

The rate constants have been found for the following radicals:

Radical	k_{15}, s^{-1}	k_{16}, litre mole^{-1} s^{-1}
$HOCH_2OO^{\cdot}$	$< 10^{5}$[108]	$1.5 \cdot 10^{10}$[108]
$HOCH(CH_3)OO^{\cdot}$	52[108]	$8 \cdot 10^{9}$[108]
$(CH_3)_2C(OH)OO^{\cdot}$	550[107], 665[108]	$5 \cdot 10^{9}$[108]
$(HO)_2C_6H_5OO^{\cdot}$	$8 \cdot 10^{3}$[109]	—
$^-OOCCH(NH_2)OO^{\cdot}$	$1.5 \cdot 10^{5}$[110]	—

The most important chemical processes involving $O_2^{\cdot-}$ are protonation and electron transfer reactions. The protonation reaction (13) is reversible. Its equilibrium constant is usually characterised by the pK for the radical $HOO^{\cdot}$. It has been shown[42,44] that the previously published values of pK($HOO^{\cdot}$) are too low and pulse radiolysis gave pK($HOO^{\cdot}$) = 4.9 ± 0.1. The heat of ionisation and hence the heat of reaction (13) are zero[44]. It has been found recently that $k_{-13} = 4.7 \times 10^{10}$ litre mole^{-1} s^{-1} [68] and $(5 \pm 1) \times 10^{10}$ litre mole^{-1} s^{-1};[94] $k_{13} = (7 \pm 2) \times 10^5$ s^{-1}.[94]

The one-electron $O_2^{\cdot-}$ oxidation reactions

$$O_2^{\cdot-} + A \rightarrow O_2 + A^{\cdot-} \tag{17}$$

in aqueous solutions have been studied mainly by pulse radiolysis. The rate constants for reactions (17) are listed in Table 2. The reactions involving the reduction of $O_2^{\cdot-}$ to the dianion of hydrogen peroxide O_2^{2-} in aqueous solutions are unknown. A combination of two processes is energetically more favourable: the protonation of $O_2^{\cdot-}$ and the reduction of the resulting peroxy-radical. Thus it has been found[67] that the rate constants for the reaction

$$QH_2 + O_2^{\cdot-} \rightarrow HOO^- + QH^{\cdot} \tag{18}$$

are $(1.3–1.7) \times 10^7$ litre mole^{-1} s^{-1} (QH_2 is hydroquinone, methylhydroquinone, or 2,5-dichlorohydroquinone).

It has been shown recently that $O_2^{\cdot-}$ can add to cobalt(II)[125] and iron(II)[120,129] complexes as well as Mn^{2+} ions[127,130] in aqueous solutions without a change in the valence of the metals. The reaction products have the structures of superperoxy- or peroxy-complexes. Analogous oxygenated complexes are formed in the reactions of $O_2^{\cdot-}$ with natural cobalt and iron complexes and their analogous (see Section VI).

3. The Reactions of $O_2^{\cdot-}$ in an Aprotic Medium

Solutions of $O_2^{\cdot-}$ in aprotic solvents can be prepared in two ways: using NaO_2, KO_2, and $R_4N^+O_2^{\cdot-}$ formed beforehand or by the electrochemical reduction of oxygen in the presence of tetra-alkylammonium salts ($R_4N^+O_2^{\cdot-}$ can be obtained by mixing K_2O and R_4NOH powders[131,132]). Furthermore $O_2^{\cdot-}$ is formed when various organic compounds (diketones,

hydroquinones, azo- and nitro-compounds, enolates, etc.) are oxidised by oxygen [133-138], for example [136]:

$$PhNO_2^-K^+ + O_2 \rightarrow PhNO_2 + KO_2 \ . \qquad (19)$$

Table 2. The rate constants for electron transfer reactions [reactions (17)] in aqueous solutions at 25°C*.

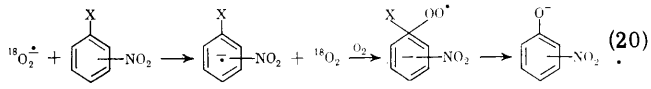
A	pH	$10^{-9}k_{17}$, litre mole^{-1} s^{-1}	References
Benzoquinone	7	1.0	93
Benzoquinone	7	0.98	66
Methylbenzoquinone	7	0.76±0.10	89
Methylbenzoquinone	7	0.80	66
2,3-Dimethylbenzoquinone	7	0.45±0.10	89
2,5-Dimethylbenzoquinone	7	0.36±0.10	89
2,5-Dimethylbenzoquinone	7	0.17; 50±10[a]	71
2,5-Dimethylbenzoquinone	—	0.75	66
2,6-Dimethylbenzoquinone	7	0.58±0.10	89
Duroquinone	7	0.023[a]	89
Duroquinone	7	0.01; 0.046[a]	66
2,5-Dichlorobenzoquinone	7	1.1	66
Menadione	7	0.038; 0.16[a]	66
2,3-Dimethylnaphthoquinone[b]	—	0.02[a]	89
Naphthoquinone-2-sulphonate	7	0.66; 55[a]	66, 71
o-Naphthoquinone	7	0.72	66
o-Naphthoquinone-4-sulphonate	7	0.84	66
Diphenoquinone	7	1.4	66
Dichloroindophenol	7	1.7±0.3	111
Indigodisulphonate	7	$9\cdot10^{-4}$; 0.029[a]	66
Tetranitromethane	5.6—6.2	1.9±0.4	112
Tetranitromethane	—	2.0	113
Tetranitromethane	—	2.0	114
$HO^\cdot$	0.46—6.75	10.1	115
CO_3^-[c]	—	0.4±0.1	43
CO_3^-	—	1.5	116
CO_3^-	—	0.28[e]	117
Br_2^-[j]	—	5.6±0.7	118
$HOO^\cdot$	—	0.085	42
$Fe(CN)_6^{3-}$	9.5—9.7	$(2.7\pm0.9)\cdot10^{-7}$	119
$KFe(CN)_6^{2-}$	9.5—9.7	$(6.2\pm0.6)\cdot10^{-6}$	119
Fe^{3+}(EDTA)	7	0.0018	120
Fe^{2+}(EDTA).OH^-	9—10	$(2\pm0.3)\cdot10^{-3}$	120
Cu^{2+}[e,k]	—	1.4	121
Cu^{2+}	—	8.4	122
Cu^{2+}	—	2.7±0.2	123
Cu^{2+}	—	1.9	124
$Cu(HCO_2)^+$	—	1.7	124
$Cu(HCO_2)_2$	—	0.3	124
$Cu(HCO_2)_3^-$	—	0.8	124
$Cu(HCO_2)_4^{2-}$	—	0.4	124
$Cu(NH_3)^{2+}$	5.8—8.5	2.2±0.6	124
$Cu(NH_3)_2^{2+}$	5.8—8.5	2.2±0.8	124
$Cu(NH_3)_3^{2+}$	5.8—8.5	1.0±0.5	124
$Cu(NH_3)_4^{2+}$	5.8—8.5	0.2±0.08	124
Cu(II)-alanine	7.4	$(2.8—3.5)\cdot10^{-3}$	124
Cu(II) glutamate	7.1	$(1—2)\cdot10^{-3}$	124
Cu(II)-glycine	7.9	$2.1\cdot10^{-3}$	124
Cu(II)-hydroxyproline	8.1	0.001	124
Cu(II)-methionine	7.1—7.8	0.006	124
Cu(II)-proline	7.5	$5\cdot10^{-4}$	124
Cu(II)-valine	6.2	0.24	124
Cu(II)-glycylglycine	6.7	0.07	124
Co(II)(4,11-diene-N_4)[f,g]	7—8	1.4	125
Co(II)(1,3,8,10-tetraene-N_4)[f,h]	7—8	1.6	125
Co(II)$(bipy)_2$[f,i]	—	1.9	125
$Mo(CN)_8^{3-}$	8.3—10.4	$(3.0\pm0.5)\cdot10^{-4}$	126
Mn^{2+}[e]	6.7	0.11±0.02	127
Mn^{2+} pyrophosphate	7.8	0.006	128

a Equilibrium constant.
b The reaction was carried out in an isopropyl alcohol–acetone mixture.
c It is suggested that CO_5^- is formed.
d Recalculated by Behar et al.[43]
e It is assumed that the reaction proceeds with formation of MO_2^+.
f It is assumed that oxygenated complexes are formed without change in the valence of the metal.
g 4,11-diene-N_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene.
h 1,3,8,10-tetraene-N_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene.
i bipy = 2,2-bipyridyl.
j Radiolysis in a flow system.
k Rotating sector method; in the remaining cases pulse radiolysis was used to determine the rate constants.

Similarly $Ru(bipy)_3^+$ reduces O_2 to O_2^- in acetonitrile with $k = 8.5\times10^8$ litre mole^{-1} s^{-1}.[139] It has been observed recently that O_2^- is formed in the decomposition of hydrogen peroxide induced by bases in pyridine[140].

It was shown in an early study[20] that KO_2 and NaO_2 in tetrahydrofuran (THF) and benzene react with acid anhydrides and chlorides via the S_N2 mechanism, forming acyl peroxides. These results have been recently confirmed[141]. It was observed[142] that the solubility of KO_2 in aprotic solvents increases sharply in the presence of crown-ethers. Subsequently it was shown that, under these conditions, KO_2 readily reacts with alkyl halides[143-145], tosylates[143,145], sulphonates[144], and esters[146]. Depending on the solvent, peroxides[144] or alcohols[143,145,147] can be formed. The latter are apparently the products of the transformations of hydroperoxides[145,148]. Using the method of "spin traps", the formation of RO$^\cdot$ radicals in the reaction of KO_2 with RHal was demonstrated; they probably arise as a result of side reactions of ROO$^\cdot$.[149] The rate constants for the reactions of KO_2 with alkyl bromides have been determined by the stopped flow method in DMSO at 25°C: 670 ± 20 litre mole^{-1} s^{-1} for MeBr, 350 ± 20 litre mole^{-1} s^{-1} for EtBr, 150 ± 10 litre mole^{-1} s^{-1} for BuBr, and 65 ± 1 litre mole^{-1} s^{-1} for iso-PrBr.[150] The authors concluded that O_2^- is apparently the most powerful nucleophile in aprotic solvents.

Like alkyl halides, aryl halides react with KO_2 to give a high yield of phenols[151,152]. However, in this case the reaction probably proceeds with electron transfer, because atmospheric oxygen is introduced into the reaction product:



(20)

Similarly, bromo- and chloro-quinolines react with KO_2 to form hydroxyquinolines[153], while bishalogenomethylarenes are converted into cyclic peroxides[154].

Somewhat earlier the nucleophilic reactions of the oxygen radical-anion were investigated using O_2^- prepared electrochemically. It was shown[155,156] that O_2^- reacts with primary alkyl halides in DMF and DMSO, forming alkyl peroxides quantitatively, and the nucleophilic substitution mechanism was proved for the first time:

$$O_2^- + AlkX \rightarrow AlkOO^\cdot + X^- \ , \qquad (21)$$

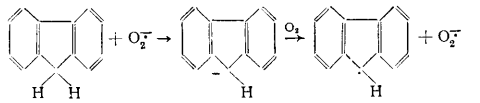
$$AlkOO^\cdot + O_2^- \rightarrow AlkOO^- + O_2 \ , \qquad (22)$$

$$AlkOO^- + AlkX \rightarrow AlkOOAlk + X^- \ . \qquad (23)$$

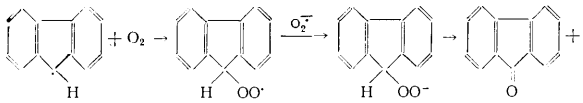
It has been shown recently[157] that reactions of the electrochemically generated O_2^- with phenyl benzoate and *p*-chlorophenyl benzoate result in the formation of aryl peroxides with rate constants of 3 ± 0.3 and 25 ± 5 litre mole^{-1} s^{-1}. $k_{21} = 1.1\times10^4$ litre mole^{-1} s^{-1} for benzyl bromide[158].

The protonation of O_2^- by phenols, carboxylic acids, and alcohols in DMF has been investigated polarographically[159]. The reaction rate constants are in the range 10^2–10^3 litre mole^{-1} and are not correlated with the pK of the proton donors. It has been pointed out[160] that the acid-catalysed disproportionation (6) is responsible for the ability of O_2^- to react with weak acids such as water. It has been suggested in a number of studies that O_2^- can abstract a hydrogen atom from compounds with an active C–H bond.

Thus the following reaction mechanism has been proposed for the chain oxidation of fluorene by the superoxide ion[73]:



(24)



(25)

The current yield of fluorenone is 5000%. Diphenylmethane is oxidised to benzophenone via an analogous mechanism (yield 400%) and 9,10-dihydroanthracene is oxidised to a mixture of anthracene and anthraquinone (yield 2000%). Apart from DMF, pyridine[45] and DMSO[161] can be used as solvents. The nucleophilic addition of O_2^- to activated double bonds has also been described; for example, benzylidenefluorene reacts with O_2^- to form fluorenenone[155] and hexa-1,3-diene and hexa-1,4-diene are converted into benzene[161]. Cyclohex-2-en-1-one forms an epoxide under analogous conditions[155]. According to the latest data, in an aprotic medium O_2^- oxidises hydrazines[162], hydrazones[162], amines[163], benzopyridine derivatives[164], and nitroalkylbenzenes[165], and reduces styrene[166].

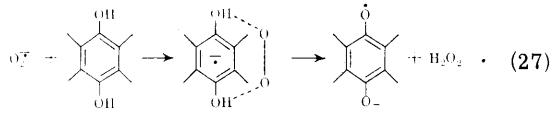
As in aqueous solutions, in aprotic solvents O_2^- readily reduces quinones (whose redox potentials are greater than that of O_2) to semiquinones. The reaction of O_2^- with benzoquinone, trimethylbenzoquinone, menadione, ubiquinones Q_0 and Q_9, tocopherylquinone, and vitamin K_1 in DMF have been investigated[80-82,167,168]. Apart from benzoquinone, the reaction is reversible in all cases. The equilibrium constants have been determined spectrophotometrically for the reactions of O_2^- with the following quinones: trimethylbenzoquinone (7.9 ± 0.6), menadione (1.5 ± 0.1), ubiquinone Q_0 (2.0 ± 0.4), ubiquinone Q_9 (2.9 ± 0.2), tocopherylquinone (1.9 ± 0.2), and vitamin K_1 (5.6 ± 0.4).[168] The closeness of the equilibrium constants to unity suggests that natural quinones can function in biological systems as traps for O_2^- (see below). One-electron reduction of quinones[169] and α-methylacridinone[170] has also been observed in reactions with KO_2; the latter readily reduces copper(II) to copper(I) in phenanthrene complexes[142] and organic copper salts[171]. The reduction of phenoxy-radicals to phenols by the superoxide ion[172] and the reaction of O_2^- with the thianthrene radical-cation[173] have also been described.

It has recently been observed[174,175] that O_2^- is capable of quenching singlet oxygen via an electron transfer reaction:

$$O_2^- + O_2(^1S) \rightarrow O_2 + O_2^- \quad . \qquad (26)$$

According to Guirand and Foote[174], $k_{26} = 1.6 \times 10^9$ litre mole^{-1} s^{-1} in DMSO. An appreciably lower value of k_{26} was found in another study[46], apparently owing to the use of an incorrect extinction coefficient[46] in the calculation of the O_2^- concentration. It is suggested that electron transfer is the first stage in the interaction of KO_2 with the chalcones $RC_6H_4COCH{=}CHC_6H_4R$[176] and tetracyclanes[177].

The possibility of the oxidation of *p*- and *o*-hydroquinones by the superoxide ion in an aprotic medium was first demonstrated in 1976.[178-180] It was observed that the reduction proceeds with the intermediate formation of semiquinone radical-anions; in particular, the semiquinones derived from catechol[178-181], trimethylhydroquinone, dopamine[167,181], adrenaline, and noradrenaline[167] were identified with the aid of electronic and EPR spectroscopy. The absence of oxygen from the reaction mixture indicates a single-stage mechanism of the formation of semiquinones[181]:



(27)

The reduction of O_2^- to O_2^{2-} by aromatic dianions with rate constants of 10^{-3} litre mole^{-1} s^{-1} at 0°C has been described[182].

The reactions of O_2^- accompanied by chemiluminescence are of special interest, primarily for biochemical research. In the initial studies by Stauff and coworkers[183,184] it was pointed out that chemiluminescence due to the formation of singlet oxygen is observed in the reaction of O_2^- with HOO· and on disproportionation of O_2^-:

$$O_2^- + HOO\cdot \rightarrow O_2(^1S) + HOO^- \quad , \qquad (28)$$

$$(O_2 \cdot O_2(^1S)) \rightarrow 2O_2 + h\nu \quad . \qquad (29)$$

According to Khan's data[185], chemiluminescence with the same origin is observed in reactions of KO_2 with anthracene, fluorescein, etc., while Arneson[186] showed that it occurs in reactions catalysed by xanthine oxidase.

Although subsequently doubt was thrown on these results[169,187,188], the formation of $O_2(^1S)$ on protonation of O_2^- was confirmed by experiments involving a specific reagent for singlet oxygen—1,3-diphenylisobenzofuran[189]. Since the formation of $O_2(^1S)$ is possible only when the heat of reaction is greater than the energy of the excitation of O_2 from the ground triplet state to the excited singlet state, the chemiluminescence due to the formation of $O_2(^1S)$ should be observed in the fastest reactions of O_2^-. Indeed, the formation of $O_2(^1S)$ in recombination reactions of O_2^- with radical-cations has been noted[190]. It is noteworthy that, as early as 1970, Dietz et al.[73] suggested that $O_2(^1S)$ is formed in the reaction of O_2^- with diphenylanthracene radical-cations. Khan[191] examined the possibility of the formation of $O_2(^1S)$ as a result of the direct disproportionation of O_2^-, but, Bielski and Allen[79] believe that this process is impossible in real systems. The formation of singlet oxygen has been recently observed in the reaction of O_2^- with diacyl peroxides[192].

Apart from $O_2(^1S)$, the chemiluminescence in the reactions of O_2^- can be due to other compounds. Thus the emission of light has been observed in the reactions of O_2^- with lucigenin[193], *N*-methylacridinone[170], luminol, and luciferin[194]. Some of these reactions were used in biochemical research for the identification of O_2^-.

IV. THE FORMATION OF O_2^- AND ITS INTERACTION WITH BIOLOGICALLY ACTIVE SUBSTRATES

Since O_2^- is present in virtually all components of the living cell, the elucidation of the sources of its formation and the probable mode of its subsequent reactions constitute an urgent problem. This section deals with reactions involving biologically active substrates; enzymatic reactions of O_2^- and interaction with haems are discussed below.

In 1969 Massey et al.[195] noted that O_2^- is formed when reduced flavins are irradiated with visible light under aerobic conditions. The reactions were inhibited by

superoxide dismutase (SOD)—an enzyme which causes the rapid dismutation of $O_2^{\cdot-}$ to O_2 and H_2O_2 (see Section V). Analogous results were obtained in another study[196] where fluorescein, eosin, Methylene Blue, and acridine were used in addition to flavins as one-electron reductants for oxygen. Photolysis resulted in the reduction of nitro blue tetrazolium, which indicated the formation of $O_2^{\cdot-}$.[197-199] The one-electron reduction of oxygen by flavin radicals and reduced flavins was studied by pulse radiolysis and photolysis in water[200-202] and by the stopped flow method in DMF[203]. Fluorescein, tryptophan, and $NADPH_2$ are capable of initiating the formation of compound III of lactoperoxidase (Fe^{3+}-complex of $O_2^{\cdot-}$) on irradiation under aerobic conditions[204]; this reaction is inhibited by SOD. It has been shown[205] that $O_2^{\cdot-}$ is formed in the aerobic oxidation of $NADH_2$ by phenazine methosulphate. The methods described are widely used nowadays for the generation of $O_2^{\cdot-}$ in biochemical experiments.

Other procedures for the generation of $O_2^{\cdot-}$ are also known. It has been shown that $O_2^{\cdot-}$ is formed in the photolysis of water and by its treatment with ultrasound[206,207], in the decomposition of K_3CrO_8 in aqueous solutions[208], and in the photolysis of aqueous CdS suspensions[209]. It has been observed with the aid of SOD that $O_2^{\cdot-}$ is formed in the oxidation of pyrogallol[210], thiols (dithiothreitol, mercaptoethanol, and glutathione)[211], 2-amino-4-hydroxy-6,7-dimethyl-5,6,7,8-tetrahydropteridine and a natural cofactor (tetrahydrobiopterin)[212-214], phenylhydrazine[215], a number of cytotoxic agents (6-hydroxydopamine, 6-aminodopamine, dialuric acid, etc.)[216-218], hydroxylamine[219,220], and dihydroxyfumaric acid[221] and in the photolysis of solutions of tryptophan[222,223], dianisidine[224], and phenoxazine derivatives[225]. The formation of $O_2^{\cdot-}$ in the oxidation of the radical-cation of the herbicide paraquat (1,1-dimethyl-4,4-bispyridinium ion) is biologically important (see Section VII)[226]. Evans et al.[227] questioned the possibility of this reaction but subsequent studies[228,229] confirmed the initial conclusions[226].

The study of reactions of $O_2^{\cdot-}$ with biologically active substrates is of particular importance, because the mechanism of the toxic effects of $O_2^{\cdot-}$ in living organisms and the possibility of combatting them can be discovered in this way. In this connection there has been much interest shown in the reactions of $O_2^{\cdot-}$ with natural hydroquinones, whose mechanism in an aprotic medium was examined previously (see Section III). As early as 1970 Miller observed[198] that *o*-dihydroxybenzenes (catechol, Tiron, and 3,4-dihydroxybenzoic acid) inhibit the reduction of cytochrome *c* by the superoxide ion. It has been shown[230] that $O_2^{\cdot-}$ generated by xanthine oxidase oxidises adrenaline to adrenochrome. This reaction has become an important method for the identification of $O_2^{\cdot-}$ in biological systems. However, one must bear in mind that the oxidation of adrenaline and other catecholamines entails the formation of $O_2^{\cdot-}$.[231,232] Subsequently the reactions of $O_2^{\cdot-}$ with *o*-dihydroxybenzene were investigated by pulse radiolysis[233,234].

α-Tocopherol is not oxidised by the oxygen radical-anion in an aqueous solution[235,236]. However, this is probably due to the low solubility of tocopherol, because $O_2^{\cdot-}$ reacts with its water-soluble analogue in water[235] and with 6-hydroxy-2,2,5,7,8-pentamethylchroman in THF.[237] It has been shown recently[167] that both tocopherol and tocopheryl acetate are capable of reacting with $O_2^{\cdot-}$ in DMF. Ascorbic acid reacts with $O_2^{\cdot-}$ can be formed in the oxidation of ascorbic acid[238]. However, the identification[239] of $O_2^{\cdot-}$ in this process was erroneous[240] and ascorbic acid is therefore an effective "trap" for the superoxide ion. Thiols can also function as traps for $O_2^{\cdot-}$.[236,241] The generally accepted mechanism of these reactions involves two stages with the intermediate formation of a neutral semiquinone:

$$AH_2 + O_2^{\cdot-} + H^+ \rightarrow AH^{\cdot} + H_2O \quad , \qquad (30)$$

$$AH^{\cdot} + O_2^{\cdot-} + H^+ \rightarrow A + H_2O_2 \quad . \qquad (31)$$

However, one must bear in mind the possibility of reactions with the formation of radical-anions, as was shown for analogous processes in an aprotic medium (see Section III).

Yang[242] showed in 1970 that the oxidation of methionine by sodium bisulphite under aerobic conditions is inhibited by SOD, which led him to suggest the involvement of $O_2^{\cdot-}$ in this reaction. (However, according to the latest data[243], $O_2^{\cdot-}$ is capable of reacting with methional to only a slight extent.) The involvement of $O_2^{\cdot-}$ in the sulphoxidation of ethionamide (2-ethyl-4-thioisonicotinamide—an active second-order tuberculostatic agent) by the $NADH_2$–phenazine methosulphate system and in the corresponding enzymatic process has also been suggested[244]. The possibility of the specific interaction of $O_2^{\cdot-}$ with model lipid membranes, due to the attraction of $O_2^{\cdot-}$ to the positively charged side of the membrane, has been demonstrated[245].

Table 3. Rate constants for the reactions of biologically active substrates and enzymes with $O_2^{\cdot-}$ and O_2.

A	k, litre mole^{-1} s^{-1}	Refs.	A	k, litre mole^{-1} s^{-1}	Refs.
$A^{\cdot-} + O_2 \rightarrow A + O_2^{\cdot-}$			$O_2^{\cdot-} + A(AH_2) \rightarrow O_2 + A^{\cdot-}$ and $HOO^- + AH^{\cdot}$		
NAD	$1.9\cdot10^9$	252	Adrenaline[c]	$4.0\cdot10^4$	241
NAD	$2.0\cdot10^9$	253	Adrenaline[c]	$1.7\cdot10^4$	235
Lumiflavin[a]	$1.6\cdot10^8$	200	Tyron	$5\cdot10^8$	233
Riboflavin[a]	$1.38\cdot10^9$	200	Ascorbic acid[c]	$2.7\cdot10^5$	238
FAD[a]	$5\cdot10^7$	200	Ascorbic acid	$1\cdot10^8$	233
FMN[a]	$9\cdot10^7$	200	Ascorbate	$(1.52\pm0.1)\cdot10^5$	259
Cytochrome a_3^{II}[b]	$3.3\cdot10^7$	254	Plastocyanine[c]	$1.1\cdot10^6$	128
Cytochrome oxidase[b]	$3.3\cdot10^7$	255	Cysteine[c]	$2.7\cdot10^6$	241
LDH.NAD	10^9—10^{10}	256	Glutathione (reduced)[c]	$6.7\cdot10^5$	241
Cytochrome c^{II} c	$3\cdot10^{-2}$	72	Homocysteine[c]	$4.6\cdot10^5$	241
Cytochrome b_5^{II} c	23	257	Dithiothreitol[c]	$1.0\cdot10^6$	241
B_{12r}	$5\cdot10^7$	258	Tetrazolium Nitroblue[c]	$5.94\cdot10^4$	259
Paraquat (PQ)[d]	$6.0\cdot10^8$	227	LDH.NAD-H_2	$(1.0\pm0.2)\cdot10^5$	260
			Compound I of horse radish peroxidase	$1.6\cdot10^6$	261
			Horse radish peroxidase[c]	10^7—10^8	262
			Cytochrome c^{III} b	$1.6\cdot10^5$[f]	263
			Cytochrome c^{III}	$1.5\cdot10^6$[e]; $2.5\cdot10^5$[f]	264
			Cytochrome c^{III}	$1.1\cdot10^5$[f]	265
			Cytochrome c^{III}	$1.4\cdot10^6$[e]; $3.0\cdot10^5$[f]	266
			Cytochrome c^{III}	$6.5\cdot10^5$[e]; $2.6\cdot10^5$[f]	267
			Cytochrome c^{III}	$1.1\cdot10^6$[e]	268
			Cytochrome c^{III}	$(2.6\pm0.2)\cdot10^5$	259
			HbO_2[c]	$4\cdot10^3$	269
			metHb[c]	$6\cdot10^3$	269

a,b,cMethods of flash photolysis, stopped flow, and competition kinetics were used to determine k respectively; in the remaining cases pulse radiolysis was used.
d $PQ^{\cdot} + O_2 \rightarrow PQ^{2+} + O_2^{\cdot-}$.
e pH ~ 7.
f pH ~ 8.4.
g pH 9.

The possibility of the interaction of $O_2^{\cdot-}$ with H_2O_2 (the "Haber–Weiss reaction")—a process ensuring the formation of the hydroxy-radical in living cells, i.e.

$$O_2^{\cdot-} + H_2O_2 \rightarrow O_2 + HO^- + HO^{\cdot} \qquad (32)$$

has been studied in a number of investigations. In contrast to the initial hypothesis, the rate of reaction (32) is extremely low according to the latest data[246-248] (although

the reaction between O_2^- and t-BuOOH is possible[249]). However, HO· is apparently formed in the presence of iron or copper complexes[248,250,251]:

$$O_2^- + M^{n+1} \rightarrow O_2 + M^n \quad , \tag{33}$$

$$M^n + H_2O_2 \rightarrow M^{n+1} + HO^- + HO\cdot \quad . \tag{34}$$

The rate constants for reactions of biologically active substrates and enzymes with O_2^- and O_2 are listed in Table 3.

V. THE PARTICIPATION OF O_2^- IN ENZYMATIC OXIDATION-REDUCTION PROCESSES

1. The Participation of O_2^- in Reactions Catalysed by Dehydrogenases, Oxygenases, Hydroxylases, and Peroxidases

In the early studies by Fridovich and Handler[4-6] the hypothesis of the formation of O_2^- in reactions catalysed by milk xanthine oxidase (EC 1.2.3.2)‡—an enzyme under the action of which xanthine is oxidised to uric acid—was based on the ability of the system to initiate the oxidation of sulphite. It was suggested that the O_2^- involved in the reaction is bound to an enzyme. Subsequently a specific enzyme—superoxide dismutase (SOD, EC 1.15.1.1), capable of inducing rapid dismutation of O_2^-—was discovered[271,272]. O_2^- was identified by EPR directly in the reaction of xanthine with xanthine oxidase (XO)[27,28] and also in the oxidation of reduced tetra-acetylriboflavin[263] and ferredoxin[273]. Gray et al.[28] used isotopically substituted oxygen for the final identification of O_2^- in reactions.

The problem of which XO active centres are responsible for the formation of O_2^- was discussed in the literature for a number of years. Massey et al.[195] showed that under aerobic conditions reduced flavins readily reduce cytochrome *c*, the reaction being inhibited by SOD. It has also been shown[273,274] that, after the removal of flavin, XO is incapable of producing O_2^-. On this basis, it was concluded that O_2^- is generated in XO by flavin-adenine dinucleotide (FAD). However, it has been found[275,276] that the rate of generation of O_2^- by ferredoxin is higher by a factor of approximately 12 than the rate of generation by flavins.

A recent careful analysis of the inter-relations between various electron transferring agents in XO showed[277,278] that the oxidation of the reduced enzyme by oxygen consists of two stages; the first, rapid stage, during which five electrons are transferred to oxygen, is due to the interaction of oxygen with a flavin, while the second, slow stage, in which one electron is transferred, is due to the interaction of oxygen with ferredoxin. The authors proposed the following process mechanisms:

$$FADH_2 + O_2 \rightleftarrows FADH_2 \cdot O_2 \, , \tag{35}$$

$$FADH_2 \cdot O_2 \rightarrow FADH \ldots O_2^- + H^+ \, , \tag{36}$$

$$FADH_2 \ldots O_2^- + H^+ + e \xrightarrow{\text{very fast}} FAD\text{-}H_2 \ldots O_2^- \, , \tag{37}$$

$$FADH_2 \ldots O_2^- \xrightarrow{\text{very fast}} FAD\text{-}H\cdot + H_2O_2 \, , \tag{38}$$

$$FADH \ldots O_2^- \rightarrow FADH\cdot + O_2^- \, , \tag{39}$$

$$FADH \ldots O_2^- + H^+ \rightarrow FAD + H_2O_2 \quad . \tag{40}$$

As already stated, the reactions catalysed by XO are accompanied by chemiluminescence[186], which indicates the accumulation of O_2^- in the course of the first three minutes of the reaction[279]. However, the source of the luminescence has not been established[280].

It is natural to suppose that xanthine oxidase cannot be the only enzyme generating O_2^-; the latter should undoubtedly be formed also in other enzyme systems. As early as 1969 it was suggested[281] that O_2 can be reduced to O_2^- in any biological system with strong reducing properties.

Massey et al.[282] postulated that three groups of flavoproteins—dehydrogenases (participating in dehydrogenation processes), oxygenases (under the action of which two oxygen atoms are introduced into the substrate), and hydroxylases (which introduce the hydroxy-group into the substrate)—are capable of reacting with O_2 in their reduced form, forming peroxy-compounds FlOOH, but the latter decompose into a flavosemiquinone and O_2^- only in the case of dehydrogenases. This view concerning the structure of the intermediate compounds of dihydroflavins with oxygen has been generally accepted[283], but later it was suggested that a charge-transfer complex and not a hydroperoxide decomposes into a semiquinone and O_2^-.[284]

The ability of dehydrogenases to generate the superoxide ion has been demonstrated in a number of studies. Massey et al.[195] observed that SOD inhibits the aerobic reduction of cytochrome *c* by the $NADPH_2$ + lipoxidase (EC 1.13.11.12), $NADPH_2$ + glutathione reductase (EC 1.6.4.2), $NADPH_2$ + ferredoxin-NADP reductase (EC 1.6.99.4), and $NADPH_2$ + reduced NADP dehydrogenase (EC 1.6.99.1) systems, i.e., as in the case of XO, electron transfer from these systems to cytochrome *c* is achieved with the aid of the oxygen radical-anion. These data have been confirmed for the $NADPH_2$ + ferredoxin-NADP reductase system[285]. It was shown subsequently that the above enzyme system can produce O_2^- in the oxidation of ferredoxin[276], FMN, or menadione[286]. The ferredoxin–ferredoxin–NADP reductase complex can also generate O_2^-, and, according to the authors[287,288], O_2^- is formed in this case on oxidation of ferredoxin and not the flavin.

It was observed in 1969[289] that, when lactoperoxidase (EC 1.11.1.7) is added to the $NADPH_2$ + reduced NADP-cytochrome *c* reductase (EC 1.6.2.4) system, compound III of peroxidase, which is a complex of O_2^- with the enzyme, is formed. On this basis, it was concluded that reduced NADP-cytochrome *c* reductase can generate O_2^- and this was subsequently confirmed[290-292]. It has been shown[293] that at low temperatures cytochrome oxidase forms the oxygenated complex $Cu(II)Fe(II)O_2^-$.

In contrast to earlier data[195], Nakano et al.[291] showed that at pH > 9, L-aminoacid oxidase (EC 1.4.3.2) is probably capable of generating O_2^-. The involvement of O_2^- (in the form of the active complex $Cu^{2+}O_2^-$) in reactions catalysed by galactose oxidase (EC 1.1.3.9) has been demonstrated[294,295]. Earlier data[296], showing the absence of inhibition of the reaction by SOD, can be accounted for by the presence of peroxidase[295]. The O_2^- ion is formed in the oxidation of 2-nitropropane to acetone, catalysed by 2-nitropropane dioxygenase, which is indicated by the inhibition of the reaction following the addition of SOD and by its acceleration when KO_2 is added[297]. According to some data[298-300], O_2^- is formed in reactions catalysed by mitochondrial enzymes: dihydroorotate dehydrogenase (EC 1.3.3.1) (DOD) and possibly succinate dehydrogenase (EC 1.3.99.1) (SD). DOD contains flavin and non haem iron and its properties should therefore resemble those of xanthine oxidase. Indeed it has been observed[298-300] that

‡The classification of enzymes is based on the recommendations of the Commission on Biochemical Nomenclature[270].

the reduction of dichlorophenolindophenol in reactions catalysed by DOD is 30% inhibited by the addition of SOD. Although the analogous reaction involving SOD is fully inhibited by SOD, its initial rate is only 3% of the rate of oxidation of succinate to fumarate and in the presence of phenazine methosulphate SOD does not inhibit the reduction of dichlorophenolindophenol by succinate dehydrogenase. It is believed that phenazine methosulphate and oxygen compete in the interaction with the active centre of SD.

The role of lactate dehydrogenase (EC 1.1.2.3) (LDH) in the oxidation of $NADH_2$ by the superoxide ion is very interesting. It is known[301] that in the presence of protons $O_2^{\cdot-}$ can slowly oxidise $NADH_2$:

$$NADH + H^+ + O_2^{\cdot-} \rightarrow NAD + H_2O_2 \quad . \qquad (41)$$

It has been observed[302,303] that the rate of oxidation of $NADH_2$ increases sharply when $NADH_2$ is bound to LDH. The reaction proceeds via a chain mechanism (the chain length at pH 7.35 is 6.2) and is inhibited by SOD. The formation of $NADH_2$ complexes with a non-specifically binding protein (albumin) did not accelerate the oxidation. The following reaction mechanism was proposed[256,260]:

$$LDH + NADH \rightleftarrows LDH.NADH \quad (K = 10^{-6} \text{ litre mole}^{-1}), \qquad (42)$$

$$LDH.NADH + H^+ + O_2^{\cdot-} \rightarrow LDH.NAD^{\cdot} + H_2O_2 \quad [k_{43} = (1.0 \pm 0.2) \cdot 10^4 \text{ litre mole}^{-1}\,s^{-1}], \qquad (43)$$

$$LDH.NAD^{\cdot} + O_2 \rightleftarrows LDH.NAD^+ + O_2^{\cdot-} \quad (k_{44} = 10^9 - 10^{10} \text{ litre mole}^{-1}\,s^{-1}), \qquad (44)$$

$$LDH.NAD^+ \rightleftarrows LDH + NAD^+ \quad (K = 10^{-4} \text{ mole litre}^{-1}). \qquad (45)$$

As already pointed out, according to Massey et al.[282] oxygenases and hydroxylases should generate $O_2^{\cdot-}$ much less effectively than dehydrogenases. However, one must bear in mind that here one is dealing with a comparison of the activities of flavins forming part of the composition of the enzyme; naturally, there exist also other active centres generating $O_2^{\cdot-}$ (for example haems and non-haem iron).

Brady et al.[304] pointed out the possibility of activating tryptophan oxygenase (EC 1.13.11.11) by the oxygen radical-anion, but they thought that such activation was insignificant. However, it has been shown in a number of studies[305-311] that $O_2^{\cdot-}$ is a substrate in reactions catalysed by this enzyme, forming with haemin an oxygenated complex, whose decomposition in the presence of tryptophan leads to the formation of the reaction product—formylkynurenine. It has been observed[312] that luciferin is oxidised by electrolytically produced $O_2^{\cdot-}$ to hydroxyluciferin. It is believed[312] that $O_2^{\cdot-}$ is also involved in the oxidation of luciferin by luciferase from *Pholas dactylus*. However, this reaction is not inhibited by SOD because, according to the authors, $O_2^{\cdot-}$ is bound to the Fe^{3+}-form of the enzyme. The participation of $O_2^{\cdot-}$ in the oxidation of cystamine catalysed by cystamine oxygenase has been demonstrated[313].

There is evidence for the possibility of the involvement of $O_2^{\cdot-}$ or the products of its subsequent reactions, $HOO^{\cdot}$ and $O_2(^1S)$, in the hydroxylation of aromatic compounds[314-317]. As for model systems, SOD inhibits hydroxylation in the presence of a number of enzymes. Thus it has been shown that SOD inhibits the hydroxylation of *n*-hydroxybenzoate and anthranilate by 3-hydroxybenzoate 4-monooxygenase (EC 1.14.93.13) and anthranilate 3-monooxygenase (EC 1.14.16.3),[318] the oxygenation of dopamine to noradrenaline by dopamine β-monooxygenase (EC 1.14.17.1) from the adrenal gland[319], and the hydroxylation of benzphetamine by a set of three microsomal components: cytochrome "P-450", reduced NADP cytochrome "P-450" reductase, and phosphatidylcholine[320,321], i.e. in all these enzyme systems the formation of $O_2^{\cdot-}$ may be expected.

The mechanism of hydroxylation with participation of cytochrome "P-450" was studied in greater detail. Strobel and Coon[320] suggested that, among the three microsomal components mentioned above, hydroxylation is carried out by cytochrome "P-450", while reduced NADP cytochrome "P-450" reductase transfers electrons from $NADPH_2$ to cytochrome *c* and phosphatidylcholine transfers electron from $NADPH_2$ to cytochrome "P-450". However, in 1973 Coon and coworkers[322] observed that $O_2^{\cdot-}$ is formed both in the presence and absence of cytochrome "P-450", i.e. is produced by the reductase; $NADPH_2$ and the reductase can be replaced by other systems generating $O_2^{\cdot-}$, for example the XO + xanthine system. It has been shown[323,324] that, when camphor is hydroxylated by the $NADH_2$ – putidaredoxin oxidoreductase + putidaredoxin (a protein containing two iron atoms and two sulphur atoms) + cytochrome "P-450cam" from *Pseudomonas putidas*, chemiluminescence inhibited by SOD is observed. It is assumed that $O_2^{\cdot-}$ is formed in this system as a result of the oxidation of the oxygenated cytochrome "P-450cam" complex via a side reaction[325].

Earlier it had been suggested[326,327] that $O_2^{\cdot-}$ is not formed in the terminal hydroxylation of alkanes and aliphatic acids by the enzyme system consisting of rubredoxin, reduced NAD rubredoxin oxidoreductase (EC 1.6.99) and ω-hydroxylase (EC 1.14.99) from *Pseudomonas oleovorans*, because the reaction is not accelerated by XO and is not inhibited by SOD. However, May et al.[328] showed that in the presence of $NADH_2$ the above system initiates the oxidation of adrenaline inhibited by SOD, i.e. $O_2^{\cdot-}$ is generated. The hydroxylation of aromatic compounds by hydroxylases, for example, the rat liver benzopyrene 3-monooxygenase (EC 1.14.14.2) containing cytochrome "P-450", is also induced by $O_2^{\cdot-}$.[329,330]

As early as 1963 it was suggested[331] that $O_2^{\cdot-}$ is involved in reactions catalysed by peroxidases (EC 1.11.1.7). Indeed it has been shown[332-335] that the oxygenated form of myeloperoxidase and horse radish peroxidase (compound III) is the product of a reaction of the Fe^{3+}-forms of the enzymes with $O_2^{\cdot-}$. For example, compound III of myeloperoxidase is formed when the enzyme is treated with a solution of $O_2^{\cdot-}$ in DMF.[335] It has also been shown[336] that peroxidase induces the hydroxylation of coumaric acid inhibited by SOD. Compound III of peroxidase can dissociate into the Fe^{3+}-form of the enzyme and $O_2^{\cdot-}$, because it oxidises $NADH_2$ and adrenaline[334,337], both reactions being inhibited by SOD. Bielski and coworkers investigated the reaction of $O_2^{\cdot-}$ with horse radish peroxidase by pulse radiolysis[261,338] (see Table 3).

It has been suggested that $O_2^{\cdot-}$ is involved in the oxidation of $NADH_2$[339-342] and dihydroxyfumaric acid[221] catalysed by peroxidases. $NADH_2$ is apparently oxidised via an analogous mechanism by catalase in the presence of hydrogen peroxide[343]. There is a possibility of the involvement of $O_2^{\cdot-}$ in the biosynthesis of prostaglandins[344] and reactions catalysed by ceruloplasmin[345].

It has been shown that $O_2^{\cdot-}$ is formed in the mitochondria of the liver[346] and heart muscle[347-350] and in liver microsomes[351,352]. It has been stated[347] that $O_2^{\cdot-}$ is generated by a component of the mitochondrial respiratory chain localised between the sites of inhibition by antimycin and rotenone and is then converted under the influence of SOD, which protects enzymes and membranes from its toxic activity, into H_2O_2. However, approximately 20% of the total amount of $O_2^{\cdot-}$ apparently fails to react with SOD and

migrates via membranes causing the peroxidation of lipids[353].

The question of the production of $O_2^{\cdot-}$ in microsomes by flavins[354], cytochrome b_{566},[353] mitochondrial ubiquinones[355,356] and microsomal cytochrome "P-450"[357-359] and reduced NADP cytochrome *c* reductase[360,361] needs to be considered. According to the results of Bartoli et al.,[361] $O_2^{\cdot-}$ is generated in the liver microsomes of new born rats only by reduced NADP cytochrome *c* reductase, while in adult animals both the reductase and cytochrome "P-450" act with equal efficiency. However, the evidence for the formation of $O_2^{\cdot-}$ under the influence of reduced NADP cytochrome *c* reductase was recently questioned[362]. Rich and Bonner[363] believe that the formation of $O_2^{\cdot-}$ in mitochondria has no special physiological significance, constituting a "short circuit" in the electron transfer chain.

When studying the ability of mitochondria and microsomes to generate $O_2^{\cdot-}$ account must be taken of possible artefacts induced by a change in the concentration of oxygen in the experiments *in vitro*. In particular, it is unlikely that $O_2^{\cdot-}$ can be produced by ubiquinones[355,356], because both hydroubiquinones and ubiquinones are effective "traps" for the oxygen radical-anion[167,168].

2. Reactions of Superoxide Dismutase

As already stated, SOD is an enzyme which causes the dismutation of $O_2^{\cdot-}$ to H_2O_2 and O_2. Cu-containing SOD has been isolated from bovine blood erythrocytes[272]. Subsequently Mn- and Fe-containing SOD were isolated from the bacteria *E. coli*.[364] The mechanism of the interaction of SOD with $O_2^{\cdot-}$ is based on the ability of a variable-valence atom (for example a copper atom) to oxidise and reduce $O_2^{\cdot-}$ alternately in the presence of protons:

$$E\text{-}Cu^{2+} + O_2^{\cdot-} \rightarrow E\text{-}Cu^{+} + O_2 \quad , \qquad (46)$$

$$E\text{-}Cu^{+} + O_2^{\cdot-} + 2H^{+} \rightarrow E\text{-}Cu^{2+} + H_2O_2 \quad . \qquad (47)$$

It is believed[365] that one of the coordination sites of the copper atom is free and that it is the site where $O_2^{\cdot-}$ is bound. However, calculation of the redox potential of oxygen based on the thermodynamics of the interaction of SOD with $O_2^{\cdot-}$ favours an outer-sphere mechanism[71]. It has been shown that water protons are not involved in reaction (47).[366] According to the latest data[367], the most likely proton donor is the imidazole residue, which binds zinc and copper ions:

$$Zn^{II}\text{—}N\!\!\left\langle\!\!\begin{array}{l}\diagup\\ \diagdown\end{array}\!\!N\text{—}Cu^{II}\text{—}OH_2 \underset{O_2^{\cdot-}}{\overset{O_2^{\cdot-}}{\rightleftarrows}} Zn^{II}\text{—}N\!\!\left\langle\!\!\begin{array}{l}\diagup\\ \diagdown\end{array}\!\!NH\cdot Cu^{I}\text{—}OH_2 \quad . \qquad (48)$$

In a study of the optical spectra of the reduced and oxidised forms of Cu-containing SOD, Fielden et al.[368] showed that, after the addition of the $O_2^{\cdot-}$ solution, an equilibrium mixture of both forms is formed in both cases. Hodgson and Fridovich[369] demonstrated the reversibility of reactions (46) and (47) using tetranitromethane, a strong electron acceptor, to achieve a leftward shift of the equilibrium. It is believed[370] that at pH > 12 SOD binds hydroxide ions and promotes their oxidation by oxygen with formation of $O_2^{\cdot-}$. It has been shown that univalent anions (Cl^-, HO^-, etc.), capable of combining with a copper atom, are competitive inhibitors of SOD[371,372].

The rate constants for reactions catalysed by SOD have been found by pulse radiolysis, polarographically, and by the method of competitive kinetics (Table 4). Table 4 shows that $k_{46} \simeq k_{47} = (1-3) \times 10^9$ litre mole^{-1} s^{-1} and that the values of k_{46} for Cu-containing SOD are almost independent of pH. For Mn- and Fe-containing SOD, the values of k_{46} decrease with increasing pH. The activation energy for reaction (46) has been found to be 4600 cal mole^{-1}.[376]

Table 4. The rate constants (litre mole^{-1} s^{-1}) for the oxidation-reduction reactions of SOD at 25°C and pH 6–7.

Enzyme	$k_{46}\cdot10^{-9}$	$k_{47}\cdot10^{-9}$	Refs.	Enzyme	$k_{46}\cdot10^{-9}$	Refs
Cu-SOD from bovine blood erythrocytes	2.3	—	373	Mn-SOD from *E. coli***	2.0	378
				Mn-SOD from *E. coli**	0.09 (pH 9.76)	377
				Mn-SOD from chick liver mitochondria**	3.6***	378
Ditto	1.4±0.2	1.9±0.6	374			
»	1.2±0.2	2.2±0.4	375	Mn-SOD from *Bacillus stearothermophilus*	0.56	381
»	2.37±0.18	2.4	376			
»	2.6	—	123	Fe-SOD from *E. coli***	1.9	377
»*	2.3	—	377	Ditto**	0.38 (pH 10.2)	377
»**	1.9	—	378	Fe-SOD from *Photobacterium leognathi*	0.52 (pH 8)	382
»**	0.18	—	202			
»	2.6	—	379	Cu^{2+} $(lys)_2$	0.58±0.10	123
Mn-SOD from *E. coli*	1.3±0.13	1.6±0.6	380	Cu^{2+} $(gly\text{-}his)_2$	0.30±0.02	123
				Cu^{2+} $(gly\text{-}his\text{-}leu)_2$	0.21±0.02	123
				Cu^{2+} $(tyr)_2$	2.6	379

*A polarographic method was used to determine values of *k*.

**Method of competition kinetics (pulse radiolysis used in all the remaining cases).

***The values of k_{46} have been divided by 2, since the enzyme consists of four subunits instead of two.

Two $O_2^{\cdot-}$ destruction processes were observed in the reaction of Mn-containing SOD: a rapid process in which the valence of manganese changes from 3 to 2 and a slow process in which Mn^+ is formed[380]. However, it may be that Mn^{2+}- and Mn^{3+}-SOD (and not Mn^+-SOD) are also involved in the slow catalytic process but at a different hydrolytic state.[383] Only rapid reactions apparently occur *in vivo*. A linear relation has been observed[384] between lg k_{46} and $I^{1/2}$ (I is the ionic strength of the solution), whose slope is −1.5 for the ClO_4^-, SO_4^{2-}, and HPO_4^{2-} anions and −2.23 for Cl^-. It is suggested[384] that a slope of −1.50 is consistent with the Brønsted theory. However, this claim is incorrect, because in fact the species reduced in reaction (7) is not $O_2^{\cdot-}$ (as assumed in the calculations), but $HOO^{\cdot}$. The influence of electrolytes on the catalytic activity of SOD has also been studied in another investigation[385].

When SOD is used to identify $O_2^{\cdot-}$, account must be taken of the fact that Cu-containing SOD is inactivated by hydrogen peroxide[366,386,387], the inactivation being accompanied by luminescence and the reduction of cytochrome *c*. In doubtful cases one must therefore use Mn-containing SOD. The use of Fe-SOD can also lead to errors owing to the presence in it of traces of iron capable of reacting with $O_2^{\cdot-}$.[388]

The ability of SOD to induce the rapid dismutation of $O_2^{\cdot-}$ was regarded previously as a unique characteristic of this enzyme. However, as early as 1973 Sawada and Yamazaki observed[262] that peroxidase exhibits a dismutase activity. Similarly a non-specific SOD activity has been observed for galactose oxidase[389], catalase, haemoglobin, and methaemoglobin[390]. Weser and coworkers[123,379,391,392] showed that simple copper(II) chelates exhibit dismutase activities. A similar activity is apparently shown by quinoline complexes of manganese[388,393] and iron[394].

The problem of whether or not O_2^- is the sole substrate of SOD or whether the enzyme is capable of suppressing the formation of singlet oxygen has been discussed recently in the literature[395,396]. According to some data[397,398], SOD does not inhibit the reaction of singlet oxygen obtained by traditional methods. However, contrary results have been obtained by Weser and coworkers[397-402], so that the question remains obscure.

3. The Involvement of O_2^- in Photosynthesis

The problem of a possible role of O_2^- in photosynthetic processes has been discussed in a number of studies. It has been observed[403-405] that the aerobic oxidation of sulphite and the reduction of cytochrome *c* by spinach chloroplasts is inhibited by SOD. It has been suggested[403-405] that O_2^- is generated by photosystem I, because the blocking of electron transport by photosystem I led to the inhibition of the photochemical oxidation of adrenaline. Epel and Neumann[406] postulated that O_2^- is formed in the oxidation of electron acceptors with a low redox potential such as Methyl Viologen, which was confirmed by experiments using free radical traps[407]. The primary electron acceptor photosystem I apparently generates O_2^-,[403-405,408] although the involvement of ferredoxin is not ruled out[409,410]. It has been shown[411] that O_2^- is also formed on irradiation of hydrolysed chlorophyll.

The manganese(II) compounds present in chloroplasts exhibit a dismutase activity[128,412]. It has been shown[128] that manganese(II) pyrophosphate undergoes non-catalytic oxidation by the superoxide ion. It has been suggested[413] that O_2^- formed in chloroplasts can be involved in the hydroxylation of *p*-coumaric acid. According to some data[414,415], the reduction of oxygen to O_2^- by chloroplasts is stimulated by ascorbate, which oxidises O_2^- via the mechanism examined previously (see Section IV). It has been suggested[416] that O_2^- is involved in the oxidative cleavage of α,β-dihydroxyethyl(2)thiamine pyrophosphate catalysed by transketolase during photosynthesis.

VI. THE PARTICIPATION OF O_2^- IN THE OXIDATION-REDUCTION REACTIONS OF NATURAL MACROCYCLIC METAL COMPLEXES AND THEIR MODELS

The interaction of natural metal complexes, for example, porphyrin complexes of iron (haems), with oxygen can be represented in a general form by the equation

$$PFe^{II} + O_2 \rightleftarrows \underset{(I)}{PFe^{II}O_2} \rightleftarrows \underset{(II)}{PFe^{III}O_2^-} \rightleftarrows PFe^{III} + O_2^- \quad . \qquad (49)$$

Haemoglobin (Hb) and myoglobin (Mb) are known to form stable oxygenated complexes (HbO_2 and MbO_2), whereas oxygenated forms have not been observed for cytochromes (with the exception of cytochrome "o"[417]). In contrast to Co-analogues of haems, for which it has been established firmly that their oxygenated complexes have the structure of the ion pairs $Co^{III}O_2^-$,[418-432] the structure of the oxygenated complexes of haems continues to be discussed in the literature. There are data supporting both structure (I)[433-437] and structure (II)[306,332,438-443]. In a recent study[444] based on the analysis of the fluorescence spectra of MbO_2 it was concluded that there is an equilibrium between forms (I) and (II), which is displaced towards the former under the usual conditions. It has been shown in recent years that simple iron(II) complexes of porphyrins can form oxygenated structures at a reduced temperature and in the case of sterically hindered complexes at the normal temperature[437,444-450].

Eqn. (49) shows that O_2^- can be formed on decomposition of oxygenated complexes of haems. Indeed the superoxide ion has been observed in the autoxidation of oxyhaemoglobin and oxymyoglobin[451-454]. It has been shown that the oxidation of HbO_2, accompanied by the formation of O_2^-, is accelerated under the influence of phenoxides[455,456], hydroquinone, catechol[457], phenylhydrazine[455,458], menadione[458], etc. Presumably the reaction with electron donors (hydroquinones, phenoxides) involves the reduction of coordinated O_2^- to HOO^- with subsequent dissociation of the complex to methaemoglobin and HOO^-.[456] A similar reaction has been described for oxygenated cobalt complexes[460]. In the presence of electron acceptors (for example, quinones) direct one-electron oxidation of oxyhaemoglobin is possible[459]. In addition, O_2^- is formed in the flash photolysis of HbO_2[461] and in ligand substitution reactions[462,463]:

$$Hb^{II}O_2 + X^- \rightarrow Hb^{III}X^- + O_2^- \quad ; \qquad X^- = CN^-,\ N_3^-\ \text{etc.} \qquad (50)$$

The kinetics of the reaction of O_2^- with cytochrome *c* have been investigated in detail[263-268] (see Table 3):

$$O_2^- + \text{cytochrome } (Fe^{III}) \rightleftarrows O_2 + \text{cytochrome } c\,(Fe^{II}) \quad . \qquad (51)$$

The distinctive features of reaction (51) are a comparatively low rate and the dependence of the rate constant on pH. It is believed[267] that the low rate of this reaction can be accounted for by the involvement of water molecules in the transition state; according to Koppenol et al.,[268] O_2^- attacks the edge of the porphyrin ring. The reaction proceeds without the formation of an intermediate complex[266,267]. The dependence of the rate constant on pH is apparently due to the change in the conformation of cytochrome[266,267], but the result may be distorted by the influence of the ionic strength[268]. Apart from cytochrome *c*, O_2^- is capable of reducing its derivatives, for example, acetylated cytochrome *c*.[464]

The autoxidation of ferrocytochrome *c* is a slow reaction ($k_{-51} = 3 \times 10^{-2}$ litre mole^{-1} s^{-1} [72]). As was to be expected, SOD accelerates autoxidation, causing a rapid dismutation of O_2^-.[465,466] Cytochrome b_5, whose reduction potential is lower by 200 mV than that of cytochrome *c*, is oxidised with formation of O_2^- but at a much lower rate (the rate constant is 23 litre mole^{-1} s^{-1}).[257] In conformity with Eqn. (49), the reaction of O_2^- with metHb results in the formation of HbO_2,[269,467-469] but there is no reaction with $metHb_4$.[469] At the same time O_2^- can oxidise HbO_2 to metHb, evidently via the mechanism examined above[269,467,470,471]. In contrast to normal haemoglobin, the reaction of O_2^- with unstable haemoglobins results in the oxidation of thiol groups and the formation of dimers[467].

The study of the mechanism of the interaction of O_2^- with natural metal complexes and their models in an aprotic medium has begun recently. It is of particular importance, because real biochemical processes involving haems take place in a hydrophobic environment. As early as 1973 Ellis and Pratt[472] showed that O_2^- forms at −50°C an oxygenated complex with hydroxocobalamin (vitamin B_{12a}) in DMF. Analogous observations were made also for the reaction of O_2^- with the dimethyl ether of Fe(III)-protoporphyrin IX.[473] It has been shown recently[474] that at room temperature O_2^- reduces Co(II)-phthalocyanine ($Co^{II}Pc$) to $Co^{I}Pc$, while the reaction of O_2^- with Co(II)-tetraphenylporphyrin ($Co^{II}TPP$) leads to the formation of the dinuclear complex $TPPCo^{II}OOCo^{II}TPP$,[475] although $Co^{I}TPP$ is also formed as an intermediate. In aqueous solutions O_2^- is

apparently incapable of reducing cyanocobalamin[258], but it reacts in DMF at room temperature with both hydroxy- and cyano-cobalamin, the former being reduced to the Co(II)-form (vitamin B_{12r}).[476] The final reaction products are probably dinuclear peroxy-complexes in both cases[475].

Like cyanocobalamin, haemin chloride is not reduced by the oxygen radical-anion in aqueous solutions[477], but the reaction does proceed in DMF, a new oxygenated haem complex, having the structure $PFe^{II}O_2^-$ or $PFe^{II}(O_2^-)_2$ being formed in the presence of a large excess of O_2^-.[478] The reliability of the identification of the oxygenated complex in the reaction of O_2^- with the dimethyl ether of protoporphyrin IX[473] is questioned in the same investigation[478]. The reduction of Mn(III)-tetraphenylporphyrin by the oxygen radical-anion in DMSO at room temperature[479] and the formation of the oxygenated complex $ZnTPPO_2^-$ in the reaction of KO_2 with ZnTPP[480] have also been described.

VII. THE TOXIC EFFECT OF O_2^- AND ITS INVOLVEMENT IN PATHOLOGICAL PROCESSES AND PHAGOCYTOSIS

Presumably the O_2^- formed in enzymatic reactions is capable of involvement in side reactions with its immediate environment and exerts thereby a toxic effect on the cell structure. As early as 1969, it was suggested[272] that SOD plays a protective role against the toxic effect of O_2^- in the organism. It was shown subsequently[481] that, when the microorganisms *Str. faecalis* and *E. coli* are grown under oxygen pressure up to 20 atm, the content of SOD increases sharply. The suppression of the synthesis of SOD by puromycin led to a decrease of the number of viable cells. The addition of SOD increased the lifetime in an oxygen medium of *E. coli* cells grown anaerobically and also suppressed the toxic effect of streptonigrin on the latter[482,483], which demonstrates, according to the author, the ability of streptonigrin to generate O_2^- under aerobic conditions. Analogous effects were observed in air and in an oxygen medium for the eukaryote *Saccharomyces cerevisiae*, grown under anaerobic conditions[484].

It has been shown that an increase of the activity of SOD in erythrocytes assists the survival of new born babies[485]. The liver of rat embryos does not contain SOD and its formation is induced by respiration[486]. The radioprotective action of SOD has been discovered recently. It was found that oxygen increases the lethal effects of radiation of cells (apparently in consequence of the formation of O_2^-), while SOD increases their resistance[487-493].

As already stated, *E. coli* cells contain Mn- and Fe-SOD. It has been found[364] that Mn-SOD is localised in the cell matrix and protects the organism from the action of endogenic O_2^-, while Fe-SOD, present in the periplasm, offers protection against exogenic O_2^-. It has been shown[494,495] that the pulmonary toxicity of oxygen is due to the formation of O_2^-. The damage to lungs due to this cause can occur during the oxidation of the herbicide paraquat[496,497], the ability of which to generate O_2^- has also been demonstrated in other biological objects[498,499] (see also Section IV). In order to reduce the effect on the lungs of the O_2^- generated during smoking, it has been suggested that SOD be used as a medicinal preparation[500]. Furthermore, O_2^- can cause the oxidative degradation of ribonuclease and the autoxidation of lysyl-tRNA synthetase (EC 6.1.1.6)[501], can reduce the level of glutathione in cells with a deficiency of glucose-6-phosphate dehydrogenase[502], and can inactivate DNA[503].

Various mechanisms of the toxic effect of O_2^- have been considered in the literature. In a number of studies it has been suggested that O_2^- or the singlet oxygen formed as a result of its dismutation are involved in the peroxidation of lipids[400,504-512]. However, it may be that O_2^- participates in the peroxidation of lipids only indirectly by reducing the complex Fe^{3+}-ADP to Fe^{2+}-ADP, which then reacts with lipids[513,514]. It has been shown[515] that O_2^- cannot react directly with cholesterol—an important component of lipid membranes. It has been postulated that O_2^-, formed in the autoxidation of menadione[459,502], 1,4-naphthoquinone-2-sulphonate[516], phenylhydrazine[455,458,502,517], dialuric acid[217], and dihydroxyfumaric acid[518,519], induces the haemolysis of erythrocytes. However, it is more likely that the true haemolytic agents are HO$^\cdot$, $O_2(^1S)$, and H_2O_2,[520-522] formed as a result of secondary reactions of O_2^-.

It has been observed that the reactions of O_2^- with catecholamines[167], cobalamins, and their models[125,475] lead to the formation of stable compounds, which are apparently no longer capable of participating in the normal metabolic processes. This has been confirmed in a study[523] where it was observed that the interaction of O_2^- with catecholamines in rat liver microsomes induces the covalent binding of catecholamines to proteins, which may be the cause of hepatitis. The ability to generate O_2^- is probably the cause of the toxic effect of 6-hydroxy- and 6-amino-dopamines[217] and of β-lapachone[524].

It has been shown recently[525] that O_2^- causes a decrease in the viscosity of the synovial fluid as a result of the depolymerisation of hyaluronic acid, which, according to the author, leads to the development of inflammatory arthritis; SOD inhibits this process and can therefore be used in the treatment of such diseases. There is also other evidence for the involvement of O_2^- in inflammatory processes[526-528] and certain anti-inflammatory drugs and their derivatives (copper complexes of salicylic acid[171,529], and penicillamine[530], corticosteroids[527,528], and others) are capable of interacting effectively with O_2^-. However, according to some data[351], corticosteroids do not inhibit and actually promote the formation of O_2^-. Na_2PtCl_6 exhibits a similar activity[531]. The formation of O_2^- in inflammatory processes can be the cause of the aggregation of thrombocytes and the liberation of serotonin[532].

Tyler observed[533] that O_2^- can inhibit the activity of reduced NAD dehydrogenase. In order to protect the enzymes of the respiratory chain from O_2^- generated in the course of respiration, mitochondria therefore contain SOD located in the immediate vicinity of reduced NAD dehydrogenase[349]. It has been shown[534] that O_2^- generated by xanthine oxidase can induce the mobilisation of iron from ferritin.

The problem of the role of the superoxide ion in cancer is of very great interest. It has been shown[535] that O_2^- can increase the carcinogenic effect of aromatic hydrocarbons. The generation of O_2^- could be the cause of the carcinogenic effect of 4-nitroquinoline *N*-oxide[536]. There are contradictory data concerning the presence and role of SOD in tumour tissues[346,537-543]. The view has been expressed[537] that cancer tissues are more sensitive to the action of O_2^- than normal tissues. It is believed[544] that O_2^- contributes to the inhibiting effect of bleomycin on cancer tissues. The role of O_2^- in the activity of another group of anticancer antibiotics, namely adriamycin, daunomycin, etc., has been discussed in a number of studies. It was observed that these antibiotics promote the formation of free radicals[545] and accelerate the oxidation of $NADPH_2$ in microcomes[546,547] and submitochondrial

particles[548]. The formation of O_2^- has been noted in all cases, which may be the cause of the high cardiotoxicity of the above antibiotics (as a result of the peroxidation of lipids[549]).

However, the hypothesis that adriamycin and daunomycin semiquinones can reduce oxygen to the superoxide ion[546-549] was not confirmed in the study of the interaction of O_2^- with adriamycin in an aprotic medium[550]. On the contrary, it was observed that, when solutions of O_2^- and adriamycin in DMF are mixed, the adriamycin semiquinone is formed quantitatively, i.e. adriamycin behaves as an effective trap for O_2^-. Consequently, adriamycin has a relatively high redox potential, which accounts for its ability to inhibit respiration in mitochondria[551,552]. The formation of O_2^- in the presence of adriamycin is apparently a consequence of unknown side reactions.

The high reactivity of O_2^- can be responsible not only for pathological phenomena but also for the protective response of the organism against external influences. The problem of the possible involvement of O_2^- in phagocytosis is therefore widely discussed in the literature. Thus Babior et al.[553] showed that polymorphonuclear leukocytes reduce cytochrome *c*, the process being inhibited by SOD. According to the data of Johnson et al.,[554] the introduction of SOD on latex particles into phagocytic vacuoles together with the bacteria *E. coli* and *Str. aureus* leads to the complete inhibition of phagocytosis. Subsequently, the formation of O_2^- in phagocytosis was confirmed for both polymorphonuclear and mononuclear leukocytes[555-567], macrophages[568,569], and blood plasma[570]. The generation of O_2^- by human blood thromobocytes has also been observed[571]. O_2^- can be regarded as one of the agents on which the bactericidal activity of leukocytes depends[572,573] although $HO^\cdot$ and H_2O_2 are apparently much more active[573,574].

Phagocytosis is accompanied by a sharply increased absorption of oxygen by granulocytes[555,576]. It is believed that an enzyme system, which employs $NADPH_2$ as the electron donor and generates O_2^-, is responsible for the respiratory burst[576]. It is interesting that increased absorption of oxygen and an increased rate of production of O_2^- in phagocytosis are not observed in patients suffering from chronic granulomatosis (CGM).[577] However, the subcellular fractions of normal and CGM leukocytes generate O_2^- at the same rates[559,578]. It is therefore possible that the cause of CGM is outside the oxygen metabolic system[578].

The mechanism of the involvement of O_2^- in phagocytosis is insufficiently clear. It has been suggested that O_2^- is formed in the phagosome as a result of the enzymatic[579] or Mn^{2+}-catalysed[580] oxidation of $NADPH_2$. The system generating O_2^- is probably associated with the surface of the leukocyte[581]. However, it is not clear how the activity of the enzyme increases sharply during phagocytosis, whether its action is suppressed by virulent bacteria, or whether the latter are specially protected against O_2^-. The generation of O_2^- in phagocytosis is enhanced in the presence of sulphydryl groups, fluoride ions, cytochalasins[582,583], immunoglobulin G[563,584], aliphatic acids[585], and anionic detergents (digitonin, deoxycholate, and zymosan)[584,586-590]. The membrane sialic acid apparently plays an important role in stimulating the formation of O_2^- in phagocytosis[591], while myeloperoxidase[592] and certain local anaesthetics[593] inhibit its formation. Doubts have been expressed also concerning the reliability of certain experiments demonstrating the involvement of O_2^- in phagocytosis[594,595]. Thus the problem of the role of O_2^- in phagocytosis still awaits its final elucidation.

During the preparation of the review for the press, new studies on the chemical and biochemical properties of O_2^- were published. New methods of generating O_2^- were described: by the oxidation of Cu_2O[596] and metal ions[597], by the decomposition of H_2O_2 on metal oxides[598], by the photolysis of aqueous solutions[599], by the photolysis of CdS in non-aqueous media[600], of $Ru(bipy)_3^{2+}$,[601] and of a melamine suspension[602], and also in electrocatalysis in the presence of cobalt chelates[603]. In contrast to earlier data, it was found that O_2^- is not formed in the reaction of $NADH_2$ with phenazine methosulphate[604]. The study of the chemical properties of O_2^- is being continued, namely: nucleophilic substitution reactions with alkyl halides, peroxides[605], and esters[606], electron transfer reactions with copper(II) salicylates[607] and cytochrome *c*[608], and the interaction of O_2^- with ascorbic acid and tocopherol[609-611], hydrogen peroxide (in the presence of iron ions)[612,613], olefins[614] and ketones (in the presence of catalysts of interphase transfer)[615]. The formation of nitroxy-radicals in the reaction of O_2^- with the *N*-oxides of heterocyclic compounds[616,617] and chemiluminescent reactions of O_2^- in the presence of carbonate[618], as well as new compounds of O_2^- with Ba^{2+} and Ca^{2+}[619] and with rhodium(III)[620] and cobalt(III)[621] complexes have been described.

The generation of O_2^- by mitochondria[622,623] and microsomes[624-627] and by reduced FMN[628] and microbial nutrient solutions[629] has been investigated in a number of studies. The study of the properties of SOD and its models has been continued[630-635] and it has been shown that data concerning the involvement in catalysis of only one of the two copper atoms are apparently incorrect[636]. The involvement of O_2^- in reactions catalysed by azoreductase[637], dopamine β-hydroxylase[638], kidney diaminooxidase[639], and 2-nitropropane dioxygenase[640] has been demonstrated. A study has been made also of the participation of O_2^- in reactions of peroxidase[641,642] and *m*-hydroxybenzoate 4-hydroxylase[643], in the vitamin K-dependent carboxylation of the glutamic acid residues of prothrombin[644], in the oxidation of cytochrome oxidase by oxygen at 173 K[645], and in the inactivation of papain[646]. The role of O_2^- in photosynthetic processes was also studied[647,648].

The investigation of the reactions of O_2^- with haems[649,650], the role of O_2^- in cancer[651,652], and the involvement of O_2^- in inflammatory processes[653-657] and in phagocytosis[658-666] have been continued. The involvement of O_2^- in processes associated with the radiation-induced damage of bacteriophages[667], the haemolysis and autoxidation of oxyhaemoglobin[668,669], the damage of the membranes of erythrocytes by copper salts[670], the autoxidation of linoleic acid[671], and the degradation of hyaluronic acid[672] has been demonstrated. It has also been shown that O_2^- is able to pass through erythrocyte membranes via anionic channels[673] and that SOD plays a protective role in the tissues of the crystalline lens of the eye[674,675].

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Group-theoretical Methods in Quantum-chemical Calculations

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Group-theoretical methods used in quantum chemistry have been reviewed. The method for constructing the basis functions of the irreducible representations of finite groups by means of projection operators has been examined in detail. Particular attention has been paid to the use of the theory of permutation groups for constructing the eigenfunctions of the operator of the square of the total spin S^2 and obtaining closed equations for the matrix elements of the Hamiltonian in a state having a definite value of S. A method has been described for finding the allowed molecular states and the orders of the secular equations obtained in variation quantum-chemical calculations. The use of the mathematical apparatus of continuous groups in quantum-chemical calculations has been discussed.
The bibliography contains 60 references.

CONTENTS

I. Introduction 550
II. Symmetry groups of the Schrödinger equation. Construction of the basis functions of irreducible representations 551
III. Permutational symmetry 552
IV. Construction of antisymmetric wavefunctions which are eigenfunctions of S^2. "Spin-free quantum chemistry" 553
V. Quasi-diagonalisation of the secular equation. Determination of allowed molecular multiplets 555
VI. Calculation of the matrix elements of the Hamiltonian in a state having a definite total spin 557
VII. Spin-projected self-consistent field equations 559
VIII. Use of the apparatus of continuous groups in quantum-chemical calculations 560

I. INTRODUCTION

The methods of group theory are at present being widely used in chemistry. The application of the abstract apparatus of group theory to specific problems of the structure of molecules is based on the symmetry properties of the systems studied. Two types of symmetry can be distinguished: a) symmetry with respect to spatial transformations, and b) symmetry with respect to the permutation of identical particles. Both types of symmetry emerge from the properties of the Schrödinger equation for many-electron systems.

In addition to the symmetry with respect to the transformation of the coordinates of real three-dimensional space, for a number of problems the Schrödinger equation may exhibit symmetry with respect to the transformation of variables in a fictitious n-dimensional space. In these cases, the term latent or dynamic symmetry is used. A widely studied example is the symmetry, discovered by Fock, of the Schrödinger equation for the hydrogen atom, written in the momentum representation, in a four-dimensional space of dynamic variables.

Many familiar concepts used in quantum chemistry are based on the group-theoretical properties of many-electron systems. Thus Pauli's principle for many-electron systems is related to the forbidden character of all irreducible representations of the permutation group of the electrons except the antisymmetric. The conservation with time of various quantities characterising the state of a molecule, such as the spin, momentum, and orbital angular momentum of an isolated molecule, is related to the fact that these quantities are characterised by the irreducible representations of groups whose operations leave the Hamiltonian of the system invariant.

The introduction of the apparatus of group theory makes it possible to explain qualitatively a number of properties of the systems being considered without resorting to numerical calculations, for example to determine the degree of degeneracy and symmetry of the allowed states and the probability of quantum transitions (selection rules). At the same time, group theory simplifies the quantitative calculation considerably, since it makes it possible to obtain effective equations for calculating the matrix elements of the physical quantities being sought.

In the present review, attention is paid to both aspects of the application of the apparatus of group theory. The construction of the basis functions of irreducible representations by means of projection operators is examined in detail. This method makes it possible to standardise this procedure completely, and does not require the solution of systems of equations or the introduction of intuitive considerations for the selection of independent functions, as is often suggested in many quantum-chemical handbooks.

Particular attention is paid in the present review to the construction of the eigenfunctions of the operator of the square of the total spin S^2. In the case where spin is preserved, the antisymmetric total wavefunction, which is an eigenfunction of the operator S^2, can be represented as a linear combination of the products of coordinate and spin functions, transforming as the conjugate irreducible representations of the permutation group. This makes it possible to develop effective methods for classifying the molecular states obtained in a specific quantum-chemical calculation, that is to find the allowed types of point symmetry and the corresponding values of the electron spin (see Section V). The secular equation of the variational problem breaks down into secular equations for each molecular multiplet.

For calculating the properties of a molecule which are independent of spin interactions, it is sufficient to know only the coordinate wavefunction, the permutation symmetry of which is related unambiguously to the value of the total electron spin. This approach was proposed by the author of the present review[1-3] (the method of coordinate wavefunctions) and independently by Matsen[4,5] (spin-free quantum chemistry). The use of coordinate wavefunctions instead of Slater determinants makes it possible to obtain closed equations for the matrix elements of the Hamiltonian in states with a definite value of the spin S.

Section VI of the present review gives these expressions for the case of the configuration of non-orthogonal orbitals. The equations for the configurations of orthogonal orbitals are obtained as particular cases of the general equations. These equations are subsequently used (Section VII) to derive self-consistent field spin-projected equations for the case of an arbitrary molecular configuration containing both closed and open shells.

In addition to the traditional point groups, and also permutation groups, in recent years use has been made of unitary groups[6-9]. The final section of the present review describes an approach to the calculation for many-electron systems based on the use of the apparatus of unitary groups, and discusses its possibilities.

II. SYMMETRY GROUP OF THE SCHRÖDINGER EQUATION. CONSTRUCTION OF THE BASIS FUNCTIONS OF IRREDUCIBLE REPRESENTATIONS

All applications of group theory in quantum mechanics are based on the result obtained by Wigner[10] in 1927, often called Wigner's theorem: the wavefunctions belonging to a given energy level transform as a representation of the symmetry group of the Schrödinger equation, that is as a representation of the group whose operations leave the Schrödinger equation invariant.

The Schrödinger equation of an isolated quantum-mechanical system is invariant with respect to the operations of the following groups:

a) the group of displacements in space of the system as a whole; the irreducible representations of this group are characterised by the value of the momentum of the system,

b) the group of orthogonal transformations in three-dimensional space, consisting of rotations about any axis passing through the centre of gravity of the system, taken as the origin of coordinates, and inversion with respect to the origin of coordinates; the irreducible representations of this group are characterised by the values of the angular momentum of the system and the parity of the basis functions,

c) the group of permutations of identical particles; the characteristics of the irreducible representations of a permutation group will be discussed below.

If the system is placed in an external potential field, the symmetry groups of the Schrödinger equation are as follows:

a) the symmetry group of the external field,

b) the group of the permutations of identical particles.

In the adiabatic approximation, the motion of the electrons in a molecule can be regarded as taking place in the external field of stationary nuclei situated in equilibrium positions†. The potential field in this case exhibits the symmetry of the point group of the molecule. Thus according to Wigner's theorem, the electronic wave-functions of the molecule belonging to a given energy level should transform as the irreducible representations of the symmetry point group of the molecule and the permutation group of the electrons. There are no restrictions on possible irreducible representations of the point group, but of the irreducible representations of the permutation group of the electons, only the antisymmetric is realised. This last restriction is usually called the Pauli principle.

To find the basis function of the representation $\Gamma^{(\alpha)}$ of a given point group G of order g it is sufficient to apply the operator

$$\varepsilon_{ik}^{(\alpha)} = \frac{f_\alpha}{g} \sum_R \Gamma_{ik}^{(\alpha)}(R)^* R \tag{1}$$

to an arbitrary function ψ_0,

$$\psi_{ik}^{(\alpha)} = \varepsilon_{ik}^{(\alpha)} \psi_0 = \frac{f_\alpha}{g} \sum_R \Gamma_{ik}^{(\alpha)}(R)^* R\psi_0. \tag{2}$$

In Eqn. (2), $\Gamma_{ik}^{(\alpha)}(R)$ denotes the matrix element of the representation $\Gamma^{(\alpha)}(R)$ corresponding to the operation $R \in G$; the summation is carried out over all elements k of the group; f_α gives the dimension of the representation.

It can readily be shown[14] that for an arbitrary operation $Q \in G$

$$Q\psi_{ik}^{(\alpha)} = \sum_l \Gamma_{li}^{(\alpha)}(Q^{-1})^* \psi_{lk}^{(\alpha)}. \tag{3}$$

For unitary representations

$$Q\psi_{ik}^{(\alpha)} = \sum_l \Gamma_{li}^{(\alpha)}(Q)\, \psi_{lk}^{(\alpha)}, \tag{4}$$

that is the functions $\psi_{ik}^{(\alpha)}$ are transformed by the operations of the group according to the ith column of the irreducible representation $\Gamma^{(\alpha)}$, and the set of f_α functions $\psi_{ik}^{(\alpha)}$ with fixed index k forms the basis of the irreducible representation $\Gamma^{(\alpha)}$. Thus by changing the values of the index k it is possible to form f_α independent bases. This is realised if ψ_0 does not exhibit symmetry properties with respect to the operations of the group G. Otherwise, the result of the application of the operator $\epsilon_{ik}^{(\alpha)}$ to it may give zero. The operator $\epsilon_{ii}^{(\alpha)}$ converts the function $\psi_{ik}^{(\alpha)}$ into itself. The operators exhibiting this property are called projection operators. For these, the following operator equation is applicable:

$$\varepsilon_{ii}^{(\alpha)} \varepsilon_{ii}^{(\alpha)} = \varepsilon_{ii}^{(\alpha)}. \tag{5}$$

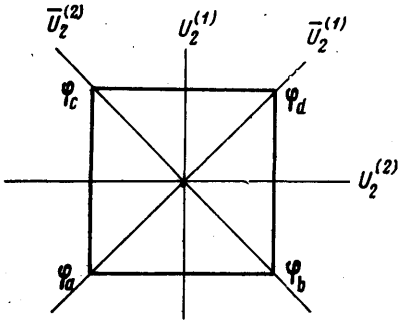
The procedure for constructing the bases of irreducible representations by means of characters[15,16], usually employed in quantum chemistry, does not make it possible to distinguish the basis functions in the case of multiple irreducible representations. Eyring, Walter, and Kimball[15] put forward a method for separating independent basis functions by solving a system of equations. Streitwieser[16] states that it is necessary to use intuition to solve this problem. The method using the projection operators (1), however, makes it possible to standardise completely the procedure for finding the bases of irreducible representations, and intuition is not required.

The effect of the operation R on the original non-symmetrised bases is found from simple geometric considerations. The original basis is broken down into separate sets in such a way that the functions belonging to a given set are transformed only into one another by the operations of the group G. These representations obviously cannot

† In a degenerate electronic state, the adiabatic approximation becomes inapplicable. Symmetrical arrangements of the nuclei now do not correspond to an energy minimum (Jahn–Teller theorem). As a consequence of electronic-vibrational interaction, instead of one minimum for a symmetrical configuration of the nuclei, there appear several minima for unsymmetrical configurations of the nuclei. The potential surface becomes multi-sheeted, and the nuclei undergo a complex motion over this surface (see Refs. 11–13 for more details).

be broader than the regular one, so that the number of times it contains an irreducible representation $\Gamma^{(\alpha)}$ is not greater than its dimension f_α. This feature makes the procedure for constructing the basis using the operators $\epsilon_{ik}^{(\alpha)}$ unambiguous, since there are f_α independent sets of operators $\epsilon_{ik}^{(\alpha)}$ differing in the value of the index k. The matrices of the irreducible representations of all the point groups and permutation groups π_3–π_6 required in order to use Eqn. (2) in specific calculations are given in a book by the author of the present review[14], which also gives examples of the construction of basis functions.

The procedure for constructing basis functions, based on the method of projection operators, can be examined for the simple example of a system of four equivalent atoms situated at the corners of a square *a*, *b*, *c*, *d*. It is assumed that an orbital of the same type is given on each atom:



This atomic configuration is invariant with respect to the operations of the point group $\mathbf{D}_4$. The four orbitals φa, φb, φc, φd form the basis of a four-dimensional reducible representation Γ of the group D_4. The characters $\chi^{\Gamma}(R)$ of this representation are equal to the number of orbitals remaining invariant on application of the corresponding operation R of the group $\mathbf{D}_4$:

R	E	C_2	$2C_4$	$2U_2$	$2\bar{U}_2$
$\chi^{\Gamma}(R)$	4	0	0	0	2

The representation Γ is readily broken down into the irreducible representations of the group $\mathbf{D}_4$ using the character tables of the irreducible representations $\Gamma^{(\alpha)}$ of the group $\mathbf{D}_4$. According to the theory of representations, the number of times the representation $\Gamma^{(\alpha)}$ appears in the breakdown of the representation Γ is given by the equation

$$a^{(\alpha)} = \frac{1}{g}\sum_R \chi^{\Gamma}(R)\,\chi^{(\alpha)}(R)^*. \qquad (6)$$

This gives‡

$$\Gamma \doteq A_1 + B_2 + E. \qquad (7)$$

The basis functions of the irreducible representations appearing in the breakdown (7) are constructed by applying the appropriate operators $\epsilon_{ik}^{(\alpha)}$ to any of the orbitals. To be specific, the orbital φa can be taken. The following are the orbitals into which the orbital φa is transformed by the eight operations of the group $\mathbf{D}_4$:

R	E	C_4	C_2	C_4^3	$U_2^{(1)}$	$U_2^{(2)}$	$\bar{U}_2^{(2)}$	$\bar{U}_2^{(1)}$
$R\varphi_a$	φ_a	φ_b	φ_d	φ_c	φ_b	φ_c	φ_a	φ_d

Character tables are sufficient for constructing the basis functions of the one-dimensional representations A_1 and B_2. To construct the basis of the two-dimensional irreducible representation E it is necessary to know its matrix elements. The matrix elements for the irreducible representations of the group D_4 are given below:

	E	C_4	C_2	C_4^3	$U_2^{(1)}$	$U_2^{(2)}$	$\bar{U}_2^{(1)}$	$\bar{U}_2^{(2)}$
A_1	1	1	1	1	1	1	1	1
B_2	1	−1	1	−1	1	1	−1	−1
E	$\begin{pmatrix}1&\\&1\end{pmatrix}$	$\begin{pmatrix}&1\\-1&\end{pmatrix}$	$\begin{pmatrix}-1&\\&-1\end{pmatrix}$	$\begin{pmatrix}&-1\\1&\end{pmatrix}$	$\begin{pmatrix}&-1\\-1&\end{pmatrix}$	$\begin{pmatrix}1&\\&1\end{pmatrix}$	$\begin{pmatrix}1&\\&-1\end{pmatrix}$	$\begin{pmatrix}-1&\\&1\end{pmatrix}$

Since each representation $\Gamma^{(\alpha)}$ appears once in the breakdown (7), in this example multiple representations do not appear. To construct the basis of the representation E, it is sufficient to use either of the two sets of projection operators: $(\epsilon_{11}^{E}, \epsilon_{21}^{E})$ or $(\epsilon_{12}^{E}, \epsilon_{22}^{E})$. This gives the following normalised functions:

$$\sigma^{A_1} = \frac{1}{2}(\varphi_a + \varphi_b + \varphi_c + \varphi_d),$$

$$\sigma^{B_2} = \frac{1}{2}(\varphi_a - \varphi_b - \varphi_c + \varphi_d),$$

$$\begin{cases}\sigma_1^{E} = \frac{1}{\sqrt{2}}(\varphi_a - \varphi_d),\\ \sigma_2^{E} = \frac{1}{\sqrt{2}}(-\varphi_b + \varphi_c).\end{cases}$$

Because of the importance of permutational symmetry in the quantum theory of many-electron systems, it will be considered separately.

III. PERMUTATIONAL SYMMETRY

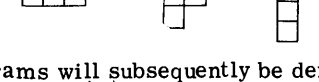
In the theory of the permutation group[14,17,18], it is shown that each irreducible representation of the permutation group of N objects, denoted π_N, can be associated with one of the partitions of the number N into integral positive terms (partition numbers). These terms are arranged in descending order:

$$\lambda^{(1)} + \lambda^{(2)} + \ldots + \lambda^{(m)} = N,\ \lambda^{(1)} \geqslant \lambda^{(2)} \geqslant \ldots \geqslant \lambda^{(m)}. \qquad (8)$$

The number of non-equivalent irreducible representations of the group π_N is equal to the number of such partitions. For example, for $N = 3$ there are three partitions:

$$3,\ 2+1,\ 1+1+1. \qquad (9)$$

The partitions (8) and (9) are represented effectively by so-called Young diagrams, in which each number $\lambda^{(i)}$ is associated with a row consisting of a number of squares equal to $\lambda^{(i)}$. Thus for $N = 3$, in accordance with Eqn.(9), three Young diagrams are possible:



The Young diagrams will subsequently be denoted by the symbol $[\lambda] \equiv [\lambda^{(1)}\lambda^{(2)}\ldots\lambda^{(m)}]$; the existence of several rows $\lambda^{(i)}$ of identical magnitude, for brevity, will be denoted by the power of $\lambda^{(i)}$. Thus the Young diagrams

‡ The point above the equality symbol indicates that this is not a literal algebraic equation; the representations in the right hand side of Eqn. (7) are contained in the representation Γ.

represented above are denoted by the following symbols: [3], [21], [1^3].

The Young diagrams characterise the symmetry of the basis functions with respect to permutation of the arguments. A Young diagram consisting of one row corresponds to a function symmetrical with respect to all its arguments; a Young diagram consisting of one column corresponds to a function antisymmetric with respect to all arguments. All other Young diagrams characterise intermediate symmetry types. There are rules which make it possible to find the matrices of the irreducible representations of the group π_N using only Young diagrams. These rules are particularly simple in the case of the so-called standard orthogonal representation§ (the Young–Yamanouchi representation[14,17]). The matrices of the standard representation for $N = 3$ are given below. In this case there are three irreducible representations, two of which are one-dimensional; $\Gamma^{[3]}(P) = 1$, and $\Gamma^{[1^3]}(P) = (-1)^p$, where p is the parity of the permutation. The representation $\Gamma^{[21]}$ is two-dimensional, and is given by the following matrices:

$$1 \quad P_{12} \quad P_{23} \quad P_{13} \quad P_{123} \quad P_{132}$$
$$\begin{pmatrix}1\\&1\end{pmatrix}\begin{pmatrix}1\\&-1\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&\frac{1}{2}\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&\frac{1}{2}\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}.$$

The basis functions of the irreducible representations $\Gamma^{[\lambda]}$ are found by applying the projection operators (1) to the non-symmetrised function Φ_0, which can be taken in the form of a product of orbitals or geminals, or in any other cluster form. In the case of a permutation group, it is more convenient to use, instead of the operator (1), the so-called Young operator¶

$$\omega_{rt}^{[\lambda]} = \sqrt{\frac{f_\lambda}{N!}} \sum_P \Gamma_{rt}^{[\lambda]}(P)\, P, \tag{11}$$

where f_λ is the dimension of the representation $\Gamma^{[\lambda]}$. The right hand side of Eqn. (11) differs from the right hand side of Eqn. (1) by a factor which is chosen in such a way that the action of $\omega_{rt}^{[\lambda]}$ on the orthonormalised product Φ_0 of one-particle functions gives a normalised function.

For representations characterised by single-row $[N]$ or single-column $[1^N]$ Young diagrams, the operator (11) is the ordinary symmetrisation or antisymmetrisation operator:

$$\omega^{[N]} = \frac{1}{\sqrt{N!}} \sum_P P, \tag{12}$$

$$\omega^{[1^N]} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p P. \tag{13}$$

It is possible to find basis functions

$$\Phi_{rt}^{[\lambda]} = \omega_{rt}^{[\lambda]}\Phi_0 = \sqrt{\frac{f_\lambda}{N!}} \sum_P \Gamma_{rt}^{[\lambda]}(P)\, P\Phi_0 \tag{14}$$

for the irreducible representations of the group π_3 in the case where Φ_0 is a product of orbitals. For the representation $\Gamma^{[21]}$ it is possible to construct two independent basis sets. This is due to the fact that the 3! functions $P\Phi_0$ in this case form the basis of a regular representation of the group π_3, and in the breakdown of the regular representation, the number of times each irreducible representation appears is equal to its dimension. Use of the explicit form of the matrix elements $\Gamma_{rt}^{[21]}$ gives:

$$\Phi^{[3]} = \frac{1}{\sqrt{6}}\{\varphi_a(1)\varphi_b(2)\varphi_c(3) + \varphi_a(2)\varphi_b(1)\varphi_c(3) +$$
$$+ \varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) + \varphi_a(2)\varphi_b(3)\varphi_c(1) + \varphi_a(3)\varphi_b(1)\varphi_c(2)\}$$

$$\Phi^{[1^3]} = \frac{1}{\sqrt{6}}\{\varphi_a(1)\varphi_b(2)\varphi_c(3) - \varphi_a(2)\varphi_b(1)\varphi_c(3) -$$
$$- \varphi_a(3)\varphi_b(2)\varphi_c(1) - \varphi_a(1)\varphi_b(3)\varphi_c(2) + \varphi_a(2)\varphi_b(3)\varphi_c(1) + \varphi_a(3)\varphi_b(1)\varphi_c(2)\},$$

$$\begin{cases} \Phi_{11}^{[21]} = \frac{1}{\sqrt{12}}\{2\varphi_a(1)\varphi_b(2)\varphi_c(3) + 2\varphi_a(2)\varphi_b(1)\varphi_c(3) - \\ \quad - \varphi_a(3)\varphi_b(2)\varphi_c(1) - \varphi_a(1)\varphi_b(3)\varphi_c(2) - \\ \quad - \varphi_a(2)\varphi_b(3)\varphi_c(1) - \varphi_a(3)\varphi_b(1)\varphi_c(2)\} \\ \Phi_{21}^{[21]} = \frac{1}{2}\{-\varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) - \\ \quad - \varphi_a(2)\varphi_b(3)\varphi_c(1) + \varphi_a(3)\varphi_b(1)\varphi_c(2)\}, \end{cases}$$

$$\begin{cases} \Phi_{12}^{[21]} = \frac{1}{2}\{-\varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) + \\ \quad + \varphi_a(2)\varphi_b(3)\varphi_c(1) - \varphi_a(3)\varphi_b(1)\varphi_c(2)\} \\ \Phi_{22}^{[21]} = \frac{1}{\sqrt{12}}\{2\varphi_a(1)\varphi_b(2)\varphi_c(3) - 2\varphi_a(2)\varphi_b(1)\varphi_c(3) + \\ \quad + \varphi_a(3)\varphi_b(2)\varphi_c(1) + \varphi_a(1)\varphi_b(3)\varphi_c(2) - \\ \quad - \varphi_a(2)\varphi_b(3)\varphi_c(1) - \varphi_a(3)\varphi_b(1)\varphi_c(2)\}. \end{cases}$$

IV. CONSTRUCTION OF ANTISYMMETRIC WAVE-FUNCTIONS WHICH ARE EIGENFUNCTIONS OF S^2. "SPIN-FREE QUANTUM CHEMISTRY"

Although the introduction of the concept of spin has made it possible to explain the chemical bond, electron spins do not take direct part in chemical bond formation; the interactions responsible for chemical bonding are purely electrostatic in character. The coordinate and spin variables in the electronic wavefunction are separated, and the function can be represented as the product of coordinate and spin wavefunctions. The fact that the energy of a system of electrons depends on the value of their total spin S is due to the existence of a unique correspondence between the permutational symmetry of the coordinate wavefunction and the value of the spin $\mathbf{S}$.

The electronic wavefunction of a molecule should satisfy three symmetry conditions:

1) the exclusion principle, that is it should be antisymmetric with respect to permutation of the electrons;

2) it should belong to one of the irreducible representations of the group of rotations in spin space, that is it should be an eigenfunction of the operator $\hat{S}^2$;

3) it should belong to one of the irreducible representations Γ^α of the symmetry point group of the molecule.

States of a molecule characterised by definite S and Γ^α are usually called electronic molecular multiplets, and denoted $^{2S+1}\Gamma^{(\alpha)}$.

To find a function satisfying the third condition, it is sufficient to use the operator $\epsilon_{ik}^{(\alpha)}$ defined by Eqn. (1). For the first two conditions to be fulfilled, instead of using the cumbersome procedure involving the construction of appropriate linear combinations of Slater determinants, it is convenient to use the apparatus of the permutation group. The representation of the complete wavefunction in the form of the product of coordinate and spin wavefunctions,

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§ The matrices of the orthogonal representation satisfy the condition:

$$\Gamma_{rt}(P^{-1}) = \Gamma_{tr}(P). \tag{10}$$

¶ The operator (11) should not be confused with the operator of symmetrisation with respect to the rows and antisymmetrisation with respect to the columns of the Young diagram, which is also often called the Young operator[17,18].

symmetrised with respect to the irreducible representations $\Gamma^{[\lambda]}$ of the permutation group, makes it possible to satisfy the first two conditions automatically. For this purpose, the coordinate and spin Young diagrams should be dual with respect to one another, that is one should be obtained from the other by interchanging rows and columns. The representation $\Gamma^{[\tilde{\lambda}]}$ ($[\lambda]$ is the Young diagram dual with respect to the diagram $[\lambda]$) is conjugate with respect to the representation $\Gamma^{[\lambda]}$, and this means that their matrix elements are related by the expression

$$\Gamma^{[\tilde{\lambda}]}_{rt}(P) = (-1)^p \Gamma^{[\lambda]}_{rt}(P), \tag{15}$$

where p is the parity of the permutation P.

It will be shown that the function

$$\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi^{[\lambda]}_r \Omega^{[\tilde{\lambda}]}_{\tilde{r}}, \tag{16}$$

where $\Phi^{[\lambda]}_r$ is a many-electron coordinate function, and $\Omega^{[\tilde{\lambda}]}_{\tilde{r}}$ is a spin function, is antisymmetric with respect to the simultaneous permutation of the space and spin variables. An arbitrary permutation $P \in \pi_N$ is applied to Eqn. (16). From Eqn. (4) it follows that

$$P\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_{u,v} \sum_r \Gamma^{[\lambda]}_{ur}(P)\, \Gamma^{[\tilde{\lambda}]}_{\tilde{v}\tilde{r}}(P)\, \Phi^{[\lambda]}_u \Omega^{[\tilde{\lambda}]}_{\tilde{v}}. \tag{17}$$

From the definition of the conjugate representation (15) and the properties of orthogonality of the matrices of the representation $\Gamma^{[\lambda]}$, it follows that

$$P\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_{u,v} \left[\sum_r \Gamma^{[\lambda]}_{ur}(P)\, \Gamma^{[\tilde{\lambda}]}_{vr}(P) \right] (-1)^p \Phi^{[\lambda]}_u \Omega^{[\tilde{\lambda}]}_{\tilde{v}} =$$

$$= \frac{1}{\sqrt{f_\lambda}} \sum_u (-1)^p \Phi^{[\lambda]}_u \Omega^{[\tilde{\lambda}]}_{\tilde{u}} = (-1)^p \Psi^{[1^N]},$$

which it was required to prove.

The symmetrised coordinate function $\Phi^{[\lambda]}_r$ is constructed, as described in the previous section, using Young operators. For a non-symmetrised function Φ_0 consisting of the product of N different orbitals, it is possible to obtain f^2_λ independent functions $\Phi^{[\lambda]}_{rt}$ which break down into f_λ basis sets, corresponding to different values of the index t.

The spin function $\Omega^{[\tilde{\lambda}]}_{\tilde{r}}$ is obtained analogously by applying the Young operator $\omega^{[\tilde{\lambda}]}_{\tilde{r}\tilde{t}}$ to the product of the one-electron two-component spin functions χ_σ, which are spinors[19]:

$$\Omega_{\sigma_1,\ldots,\sigma_N} = \chi_{\sigma_1}(1)\, \chi_{\sigma_2}(2) \ldots \chi_{\sigma_N}(N). \tag{18}$$

The set of 2^N quantities $\Omega_{\sigma_1 \ldots \sigma_N}$ form a tensor of rank N in two-dimensional spinor space. On rotation of the system of coordinates, a 2^N-dimensional representation of the group of the rotations is induced in the components of Eqn. (18). This is broken down into irreducible parts by the application of the Young operators to the function (18) (see section 4-2 in Ref. 14). The spin functions obtained

$$\Omega^{[\tilde{\lambda}]}_{r,\sigma_1 \ldots \sigma_N} = \omega^{[\tilde{\lambda}]}_{\tilde{r}\tilde{t}} \Omega_{\sigma_1 \ldots \sigma_N} \tag{19}$$

for a fixed set $\sigma_1 \ldots \sigma_N$, transform as an irreducible representation of the permutation group $\Gamma^{[\tilde{\lambda}]}$, and for a fixed $\tilde{r}$ they transform as an irreducible representation $D^{(S)}$ of the group of three-dimensional rotations, that is the number of independent functions (19) with a fixed $\tilde{r}$ is equal to $2S + 1$ (this explains the absence of the index $\tilde{t}$ from the left hand side of Eqn. (19); to find one of the f_λ basis sets corresponding to the representation D^S, it is sufficient to select any fixed $\tilde{t}$ for which the application of $\omega^{[\tilde{\lambda}]}$ to $\Omega\sigma_1 \ldots \sigma_N$ does not give zero).

The spin variables for an electron take only two values. Since an antisymmetric function becomes zero when the variables coincide, the spin Young diagrams for electrons cannot contain more than two squares in a column, that is the spin diagram $[\tilde{\lambda}]$ contains not more than two rows. If the projection of the spin of the electron in one square of a column of the spin Young diagram is 1/2, the projection of the spin of the electron in the other square should be equal to −1/2, that is the spins of these electrons are paired. It is obvious that a contribution to the total spin of the system will be made only by unpaired spins, the number of which is determined as the difference in the rows of the Young diagram ($\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)}$). Thus the value of the total spin corresponding to the function (19) is defined unambiguously by the spin Young diagram $[\tilde{\lambda}]$ and is equal to†:

$$S = \frac{1}{2}(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)}), \tag{20}$$

where $\tilde{\lambda}(i)$ is the length of the ith row, and the value of the projection of the spin is determined from the equation

$$M_S = \sum_{i=1}^{N} \sigma_i. \tag{21}$$

Thus for example for three electrons, two independent spin functions, transforming as the representation $\Gamma^{[21]}$ of the group π_3 and describing the state with $S = 1/2$ and $M_S = 1/2$, are found by applying the Young operator $\omega^{[21]}_{\tilde{r}\tilde{t}}$ to $\Omega_{\frac{1}{2},\frac{1}{2},-\frac{1}{2}} \equiv \alpha(1)\alpha(2)\beta(3)$. Since the matrices of the representation $\Gamma^{[21]}$ are related to the matrices of the representation $\Gamma^{[21]}$ (Russian page 1033) by Eqn. (15), it follows that

$$\Omega^{[21]}_{1,\alpha\alpha\beta} = \frac{1}{\sqrt{2}} [-\alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)],$$

$$\Omega^{[21]}_{2,\alpha\alpha\beta} = \frac{1}{\sqrt{6}} [2\alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3)].$$

In quantum chemistry, the term covalent structure is used to describe a configuration of atoms with one valency electron on each atom, characterised by a definite way of combining the spins of the valency electrons to give the total spin S. The number of such ways determines the number of independent covalent structures with spin S. In classical textbooks of quantum chemistry, it is determined by the so-called Rumer rule[15]. Since a configuration of valency electrons is in fact a configuration of singly-filled orbitals, the wavefunction describing it can be written in the form

$$\Psi^{[1^N]}_t = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi^{[\lambda]}_{rt} \Omega^{[\tilde{\lambda}]}_{\tilde{r}}, \tag{22}$$

† This unique correspondence between the Young diagram and the total spin applies only to particles having a spin of 1/2. For particles having $s > 1/2$, several values of S may correspond to the permutational symmetry of the given Young diagram. Thus if the spin of the particle $s = 1$, the diagram[31] corresponds to values of the total spin $S = 1, 2, 3$.[14]

where the subscript t numbers the independent states, the number of which is equal to the dimension f_λ of the irreducible representation $\Gamma^{[\lambda]}$. The expression for f_λ is written in terms of N and S [14]:

$$n(N, S) \equiv f_\lambda = \frac{N!\,(2S+1)}{\left(\frac{N}{2}+S+1\right)!\left(\frac{N}{2}-S\right)!}. \qquad (23)$$

This is also the equation for the number of covalent structures. For example, in the case of the singlet state for the six π-electrons of the benzene molecule, there are five covalent structures (corresponding to the three Kekule structures and the two Dewar structures); for the triplet state, $n(6,1) = 9$.

In problems not involving spin interactions, it is sufficient, for a complete description of the system, to give only the coordinate wavefunction. The "memory" of spin is preserved, since it is contained in the permutational symmetry of the coordinate wavefunction. Thus for a description of covalent structures it is sufficient to give the coordinate functions $\Phi_{rt}^{[\lambda]}$ found from Eqn. (14). The use of coordinate wavefunctions is also convenient in more complex cases (see subsequent sections). This "spin-free quantum chemistry", as already noted in the Introduction, was first proposed in papers by the author of the present review[1-3] and Matsen[4,5]. This approach has been widely used in recent years[20-28].

It should be noted that calculations using the complete wavefunction in the form (16) are equally convenient in those cases where characteristics of the molecule associated with spin are being dealt with. This applies particularly to the calculation of spin density[29,30]. In the case of the calculation of spin-orbital interactions, since in non-relativistic theory these calculations are carried out using perturbation theory, it is again convenient to take the wavefunctions of the zeroth approximation in the form (16).

V. QUASI-DIAGONALISATION OF THE SECULAR EQUATION. DETERMINATION OF ALLOWED MOLECULAR MULTIPLETS

Most procedures in present-day quantum-chemical calculations are based on the one-electron approximation. In calculations taking account of the possible realisation of different orbital configurations in the system, the problem of solving secular equations of very high order arises (the order of the equations is determined by the number of many-electron states considered). The total number of states in an N-electron system with allowance for all configurations in a basis of k orbitals is equal to[14]

$$n(k, N) = \binom{2k}{N} = \frac{(2k)!}{(2k-N)!\,N!}. \qquad (24)$$

Thus the order of the secular equation obtained is very large, even for small systems. Thus for six electrons and six orbitals, $n(6,6) = 924$.

If however the states of the system are described by wavefunctions belonging to bases of irreducible representations of the symmetry group of the Hamiltonian, the secular equation is quasi-diagonalised. It follows from the Wigner–Eckart theorem[14] that if the function $\psi_{ik}^{(\alpha)}$ belongs to the kth basis of the representation $\Gamma^{(\alpha)}$ of the symmetry group of the Hamiltonian $\mathcal{H}$, then

$$\langle \psi_{ik}^{(\alpha)} | \mathcal{H} | \psi_{i'k'}^{(\alpha')} \rangle = \delta_{\alpha\alpha'}\delta_{ii'} \langle k \| \mathcal{H} \| k' \rangle^{(\alpha)}, \qquad (25)$$

where δ_{ik} is the Kronecker symbol ($\delta_{ii} = 1$, $\delta_{ik} = 0$ for $i \neq k$). The diagonal terms relating to the same irreducible representation are equal. All the non-diagonal terms become zero, except the matrix elements with functions from different bases, transforming according to the same column i; the double bar in the matrix element indicates that it is independent of the number i of the basis function.

Thus the original secular equation breaks down into equations relating to separate irreducible representations. The order of the secular equation corresponding to the representation $\Gamma^{(\alpha)}$ is equal to the total number of times $\Gamma^{(\alpha)}$ appears in the breakdown of the reducible representation induced by the original set of variation functions.

Since the Hamiltonian of a molecule is invariant with respect to permutation of the electrons, in the construction of the wavefunction from Eqn. (16) the secular equation breaks down into blocks, each of which corresponds to a definite irreducible representation $\Gamma^{[\lambda]}$ of the permutation group. As shown in the previous section, the representation $\Gamma^{[\lambda]}$ is related unambiguously to the value of the total electron spin of the system S.

Further diagonalisation of the secular equation takes place in the construction, from functions corresponding to a definite value of S, of linear combinations transforming as the irreducible representations $\Gamma^{(\alpha)}$ of the symmetry group of the Hamiltonian, that is in the construction of the eigenfunctions of the molecular multiplets ${}^{2S+1}\Gamma^{(\alpha)}$. This is achieved by applying the operators $\epsilon_{ik}^{(\alpha)}$ to the functions $\Phi_{rt}^{[\lambda]}$. The variation problem reduces to the solution of the secular equation for each multiplet.

Thus before carrying out the variation calculation it is appropriate to find all possible molecular multiplets for the given problem and the orders of the corresponding secular equations. This problem can be examined for the case of a system of N equivalent atoms, on each of which one degenerate orbital $\varphi_{m,a}^{(l)}$ is given, where a is the number of the atom, and l and m the orbital angular moment and its projection on the z axis respectively. It is assumed that the number of electrons is equal to N. The total number of non-symmetrised coordinate states, described by functions of the type

$$\Phi_{m_1 \ldots m_N}^{(l)} = \varphi_{m_1 a}^{(l)}(1)\,\varphi_{m_2 b}^{(l)}(2) \ldots \varphi_{m_N q}^{(l)}(N). \qquad (26)$$

is obviously equal to $(2l+1)^N$. The construction, from the functions (26), of the basis of the representation unambiguously related to the spin S is carried out by applying the Young operators $\omega_{rt}^{[\lambda]}$ to $\Phi_{m_1 \ldots m_N}^{(l)}$. The order of the reducible representation induced in these functions is $f_\lambda (2l+1)^N$. To find the characters of this representation, the operation of the symmetry point group (this operation, given at the origin of coordinates, is denoted $\mathfrak{R}$) is applied to the function $\omega_{rt}^{[\lambda]} \Phi_{m_i \ldots m_N}^{(l)}$. The application of $\mathfrak{R}$ to the configuration of localised orbitals reduces to the permutation P of the centres of the orbitals and the operations of the point symmetry R in the atomic system of coordinates. For the operation $\mathfrak{R}$, this corresponds to the permutation P with the cyclic structure $\{1^{\nu_1} 2^{\nu_2} \ldots k^{\nu_k}\}$, where ν_i is the number of cycles of length i, the equation for the character being sought can be written in the form[31]:

$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\,[\chi^{(l)}(R)]^{\nu_1}\,[\chi^{(l)}(R^2)]^{\nu_2} \ldots [\chi^{(l)}(R^k)]^{\nu_k}, \qquad (27)$$

where $\chi^{(l)}(R)$ is the character of the irreducible representation $D^{(l)}(R)$ of the group of orthogonal transformations of three-dimensional space corresponding to the operation of the point symmetry R.

When orbitals of different types are given on the atoms, it is possible to have several covalent configurations, differing in the permutations of orbitals between identical atoms. A contribution to the character is made only by those configurations which are transformed into themselves by the operation $\mathfrak{R}$. The number of such configurations will be noted $\tau(\mathfrak{R})$. The equation for the character has the following form:

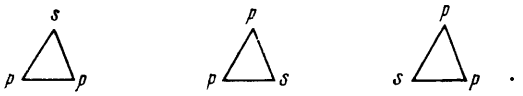
$$X^{[\lambda]}(\mathfrak{R}) = \chi^{[\lambda]}(P)\,[\chi^{(l_1)}(R)]^{\nu_1}\,[\chi^{(l_2)}(R^2)]^{\nu_2} \ldots [\chi^{(l_k)}(R^k)]^{\nu_k}\tau(\mathfrak{R}). \quad (28)$$

The orbital momenta l_i for the atoms appearing in a given cycle should coincide, otherwise the character becomes zero. If all the atoms are equivalent, and l_i are identical, it follows that $\tau(\mathfrak{R}) = 1$, and Eqn. (28) becomes Eqn. (27).

The breakdown of the representation with the characters (28) into irreducible representations $\Gamma^{(\alpha)}$ gives the allowed types of point symmetry. The corresponding values of the electron spin S, according to Eqn. (20), are determined unambiguously by the form of the spin Young diagram $[\widetilde{\lambda}]$, dual with respect to the coordinate Young diagram $[\lambda]$. This is a consequence of the fact that a unique correspondence exists between the irreducible representations $U_2^{[\widetilde{\lambda}]}$ of the unitary group $\mathbf{U}_2$, induced in the spin functions $\Omega^{[\widetilde{\lambda}]}$, and the irreducible representations $D^{(S)}$ of the group of rotations $\mathbf{R}_3$.[14] The method for finding the allowed molecular multiplets can be represented schematically as follows:

$$\begin{array}{ccc} U^{[\lambda]}_{l_1 l_2 \ldots l_k} & \leftrightarrow & U_2^{[\widetilde{\lambda}]} \\ \downarrow & & \downarrow \\ \Gamma^{(\alpha)} & \longleftrightarrow & D^{(S)} \end{array} \quad . \quad (29)$$

An example is provided by a system of three equivalent atoms, with point symmetry $\mathbf{C}_{3v}$, where p orbitals are given on two of the atoms, and an s orbital is given on the other:



Three covalent configurations are possible. The state of the system with $S = 3/2$ can be considered. This corresponds to the spin Young diagram $[\widetilde{\lambda}] = [3]$. The permutational symmetry of the coordinate wavefunction in this state is characterised by the Young diagram $[1^3]$. The group $\mathbf{C}_{3v}$ contains three classes of operation. For the identity class E, all three configurations make a contribution to the character, that is $\tau(E) = 3$. Each of the operations of the class σ_v leaves one of the configurations invariant, so that $\tau(\sigma_v) = 1$. On application of the operation C_3, the configurations are converted into one another, that is $\tau(C_3) = 0$. The permutations corresponding to the operations of the point group have the following cyclic structure:

$$\begin{array}{ccc} E & C_3 & \sigma_v \\ \{1^3\} & \{3\} & \{12\} \end{array} \quad .$$

From Eqn. (28) and the equality $\tau(C_3) = 0$, it follows that

$$X^{[1^3]}(E) = \chi^{[1^3]}(\{1^3\})\,\chi^{0}(E)\,[\chi^{(1)}(E)]^3\,\tau(E),$$

$$X^{[1^3]}(C_3) = 0,$$

$$X^{[1^3]}(\sigma_v) = \chi^{[1^3]}(\{12\})\,\chi^{(0)}(\sigma_v)\,\chi^{(1)}(\sigma_v^2 \equiv E)\,\tau(\sigma_v).$$

Since moreover $\chi^{(0)}(E) = \chi^{(0)}(\sigma_v) = 1$, $\chi^{(1)}(E) = 3$, and $\chi^{[1^3]}(\{12\}) = -1$, the characters of the reducible representation are:

$$\begin{array}{ccc} E & 2C_3 & 3\sigma_v \\ 27 & 0 & -3 \end{array} \quad .$$

Breakdown of this representation into the irreducible representations of the group $\mathbf{C}_{3v}$ gives the allowed quartets and their multiplicity 3^4A_1, 6^4A_2, 9^4E. The maximum order of the secular equation corresponds to the term ^4E and is equal to nine.

The use of the methods of group theory also makes it possible to solve a more general problem, namely to find the allowed molecular states which can be formed from given atomic states. The solution of this problem was first given by Kotani[32] and was subsequently generalised for the case of complexes of impurity ions in a crystal[33,34]. Kotani's method, however, requires the tedious calculation of the spin factor. The present author[35,36] showed that the determination of the allowed states of a system is simplified considerably by breaking down the complete wavefunction into coordinate and spin functions (16). This approach was used as a basis for the development of general methods for classifying the states of many-electron systems for given states of the sub-systems[31,37]. In these methods, the permutations of the sub-systems reduce to the permutations of particles between the sub-systems. For systems in which the number of particles $N \geqslant 10$, this is no longer effective. Since in the given problem the internal structure of the sub-system is not important, it is more natural to regard each sub-system as a single whole. This approach was developed in Refs. 38–41. The essential features of the method proposed in Ref. 39 will be described briefly.

A many-particle system consisting of n many-particle sub-systems, which may be atoms, ions, combinations of ions (ligands), etc., can be considered. From the viewpoint of the transformational properties of the wavefunction of the system of interest, each of the sub-systems can be regarded as a single particle having spin S_a. Depending on whether S_a is integral or half-integral, the sub-systems obey Bose–Einstein or Fermi–Dirac statistics, and the total wavefunction of the system is symmetric or antisymmetric with respect to permutations of the sub-systems. The wavefunction of the system, which exhibits regular permutational symmetry, can be represented in the form

$$\Psi = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi_r^{[\lambda]} \Omega_r^{[\bar{\lambda}]}, \quad (30)$$

where

$$[\bar{\lambda}] = \begin{cases} [\lambda] & \text{for boson sub-systems,} \\ [\widetilde{\lambda}] & \text{for fermion sub-systems,} \end{cases}$$

$[\widetilde{\lambda}]$, as in Eqn. (16), is the Young diagram dual with respect to the diagram $[\lambda]$.

The coordinate function with symmetry corresponding to the Young diagram $[\lambda]$ is constructed by means of the Young operators from the coordinate functions of the sub-systems, each of which belongs to a given irreducible representation $\Gamma^{(\alpha_a)}$ of the local symmetry group of the sub-system $\mathbf{G}_a$. The group $\mathbf{G}_a$ may be either the group of orthogonal transformations in three-dimensional space $\mathbf{O}_3 = \mathbf{R}_3 \times C_i$ (the sub-systems are assumed to be free) or a symmetry point group (the sub-systems are considered in an external field, usually a crystal field). The expression for the character of the reducible representation

$U^{[\lambda]}_{\alpha_1 \ldots \alpha_k}$ induced in the coordinate functions of the entire system, is analogous to Eqn. (28):

$$X^{[\lambda]}(\Re) = \chi^{[\lambda]}(P)\,[\chi^{(\alpha_1)}(R)]^{\nu_1}\,[\chi^{(\alpha_2)}(R^2)]^{\nu_2} \ldots [\chi^{(\alpha_k)}(R^k)]^{\nu_k}\tau(\Re). \quad (31)$$

The breakdown of the representation (31) into irreducible representations gives the allowed types of point symmetry. To determine the corresponding values of the total electron spin of the system S, it is necessary to break down the representation $U^{[\tilde{\lambda}]}_{^2S_a+1}$ of the unitary group $U_{^2S_a+1}$, induced in $(2S_a + 1)$-dimensional spin space in the functions $\Omega^{[\tilde{\lambda}]}_{\tilde{r}}$, into the irreducible representations of the group R_3. In contrast to the case where $S_a = 1/2$, when there is a unique correspondence of the representations $U^{[\tilde{\lambda}]}_2$ and $D^{(S)}$, in the case where $S_a > 1$ a single Young diagram can correspond to several different values of the total spin S. Tables of these quantities are given in Appendix 3 of Ref. 14.

Thus the procedure for finding the allowed multiplets can be represented schematically in the form

$$\begin{array}{ccc} U^{[\lambda]}_{\alpha_1 \ldots \alpha_k} & \leftrightarrow & U^{[\tilde{\lambda}]}_{^2S_a+1} \\ \downarrow & & \downarrow \\ \Gamma^{(\alpha)} & \longleftrightarrow & D^{(S)} \end{array} . \quad (32)$$

Since with the exception of the case where $S_a = 1/2$ the Young diagram $[\tilde{\lambda}]$ can correspond to several values of S, the procedure (32) is carried out systematically for all allowed Young diagrams of n squares, after which the sums of identical terms are taken.

An expression can readily be obtained for the characters of the reducible representation containing all terms of a given multiplicity. As shown in Refs. 38–41, the equations for the characters can be derived in terms of the coefficients of the plethysm of the unitary groups introduced by Littlewood[42]. On the other hand, the same equations are expressed in terms of the $3nj$ symbols of the group of three-dimensional rotations. As a result, it is possible to obtain a relationship between the coefficients of the plethysm and the $3nj$ symbols[39–41].

This method has been generalised for the case of spin-orbit coupling, and examples have been given for various specific systems[39–41].

VI. CALCULATION OF THE MATRIX ELEMENTS OF THE HAMILTONIAN IN A STATE HAVING A DEFINITE TOTAL SPIN

The representation of the eigenfunctions of the operator $\hat{S}^2$ in the closed form (16), instead of the linear combinations of Salter determinants, makes it possible to obtain equations for the matrix elements of a Hamiltonian not depending on spin[43] for the case of an arbitrary configuration of non-orthogonal orbitals. The coefficients in these equations include explicitly the dependence on spin, since they contain the matrix elements of the irreducible representation $\Gamma^{[\lambda]}$, unambiguously related to S. The expressions for the configurations of orthogonal orbitals usually employed are obtained as particular cases.

It is possible to give the corresponding equations for the configuration of singly-filled non-orthogonal orbitals‡:

$$K: \varphi_1\varphi_2 \ldots \varphi_N,\ \langle\varphi_a|\varphi_b\rangle = s_{ab} \neq 0, \quad (33)$$

used in the spin-projected method of "different orbitals for different spins". The non-symmetrised coordinate function of this configuration can be denoted Φ_0:

$$\Phi_0(K) = \varphi_1(1)\varphi_2(2) \ldots \varphi_N(N).$$

As a consequence of the non-orthogonality of the orbitals, the symmetrised coordinate function $\Phi^{[\lambda]}_{rt}$, obtained by applying $\omega^{[\lambda]}_{rt}$ to Φ_0, must be normalised:

$$\Phi^{[\lambda]}_{rt} = N^{[\lambda]}_t(K)\,\omega^{[\lambda]}_{rt}\Phi_0(K). \quad (34)$$

It can readily be shown[44] that the normalisation factor $N^{[\lambda]}_t(K)$ is given by the following equation:

$$[N^{[\lambda]}_t(K)]^{-2} = \sum_P \Gamma^{[\lambda]}_{tt}(P)\,\langle\Phi_0(K)|P\Phi_0(K)\rangle = \\ = 1 + \sum_{P_{ab}} \Gamma^{[\lambda]}_{tt}(P_{ab})\,s^2_{ab} + \sum_{P_{abc}} \Gamma^{[\lambda]}_{tt}(P_{abc})\,s_{ac}s_{ba}s_{cb} + \ldots \quad (35)$$

The index t numbers the different states, differing in the way in which the spins of the individual electrons are combined to give the total spin S. The number of such states is equal to f_λ. The average value of the Hamiltonian for the configuration (33) and a particular choice of ways of combining the electron spins was obtained by Goddard[20] using the apparatus of the permutation group. The equations in Goddard's paper are very complex, however. Gerratt[23] (see also Ref. 44) obtained much more compact expressions for an arbitrary way of combining the spins. Since the Hamiltonian of a molecule is the sum of one-electron and two-electron operators

$$\mathcal{H} = F + G = \sum_{i=1}^{N} f_i + \sum_{i<j}^{N} g_{ij}, \quad (36)$$

expressions can be given for the matrix elements of the operators F and G. These matrix elements can be represented as follows:

$$\langle Kt|F|K\tilde{t}\rangle^{[\lambda]} = N^{[\lambda]}_t(K)\,N^{[\lambda]}_{\tilde{t}}(K)\sum_{a,b} N^{[\lambda]}_{t\tilde{t}}(K_a, K_b)\,f_{ab}, \quad (37)$$

$$N^{[\lambda]}_{t\tilde{t}}(K_a, K_b) = \sum_{P'} \Gamma^{[\lambda]}_{t\tilde{t}}(P'P^{ia}_b)\,\langle\Phi_0(K_a)|P'\Phi_0(K_b)\rangle, \quad (38)$$

where K_a is the configuration obtained from the configuration K by removing the orbital φ_a; the permutation P^{ia}_b moves the electron of the orbital φ_a into the orbital φ_b in the function $\Phi_0(K)$; the permutations P' belong to the group π_{N-1}, obtained from π_N by removing the electron i_a; and $f_{ab} = \langle\varphi_a|f|\varphi_b\rangle$ is the one-electron matrix element.

$$\langle Kt|G|K\tilde{t}\rangle^{[\lambda]} = \frac{1}{2}N^{[\lambda]}_t(K)\,N^{[\lambda]}_{\tilde{t}}(K) \times \\ \times \sum_{a,b}\sum_{c,d} \gamma_{ac}\gamma_{bd}N^{[\lambda]}_{t\tilde{t}}(K_{ac}, K_{bd})\,g_{ac,bd}, \quad (39)$$

$$N^{[\lambda]}_{tt}(K_{ac}, K_{bd}) = \sum_P \Gamma^{[\lambda]}_{tt}(P''P^{ia'c}_{bd})\,\langle\Phi_0(K_{ac})|P''\Phi_0(K_{bd})\rangle. \quad (40)$$

‡ To avoid confusion, it should be emphasised that the subscripts a and b number the orbitals, and are not related to the numbering of the atoms, that is the orbital φ_a may denote either an atomic (if the valency scheme method is used) or a molecular orbital, including contributions from all the atoms.

In Eqn. (39), $\gamma_{ac} = 1 - \delta_{ac}$, which corresponds to the single filling of the orbitals of the configuration K. The permutation $P^{i_a i_c}_{bd}$ moves the electrons from the orbital φ_a to φ_b and from φ_c to φ_d; the permutations P'' belong to the group π_{N-2}, obtained from π_N by removing the electrons i_a and i_c. The two-electron matrix element is $g_{ac,bd} = \langle \varphi_a(i)\varphi_c(j)|g_{ij}|\varphi_b(i)\varphi_d(j)\rangle$.

For antisymmetric coordinate states with $[\lambda] = [1^N]$, corresponding to the maximum value of the spin, it can readily be shown that Eqns. (37) and (39) become Löwdin's familiar equations[45] for the one-determinant wavefunction constructed on non-orthogonal spin-orbitals:

$$\langle K|F|K\rangle^{[1^N]} = \frac{1}{\det|s_{mn}|}\sum_{a,b}(-1)^{i_a-i_b}\det|s_{mn}|_{ab}f_{ab}, \quad (41)$$

$$\langle K|G|K\rangle^{[1^N]} = \frac{1}{\det|s_{mn}|}\sum_{a<c}\sum_{b<d}(-1)^{i_a+i_b+i_c+i_d}\det|s_{mn}|_{ac,bd}(g_{ac,bd}-g_{ac,db}), \quad (42)$$

where $\det|s_{mn}|_{ab}$ is the minor of the determinant $\det|s_{mn}|$ obtained by deleting the ath row and the bth column.

Equations as simple as Eqns. (41) and (42) are obtained only for the case of maximum spin or for a one-determinant wavefunction, not corresponding in general to a definite value of S. For an arbitrary spin, it is necessary to use Eqns. (37)–(40). The calculation of the non-orthogonality coefficients $N^{[\lambda]}_{tt}(K_a, K_b)$ and $N^{[\lambda]}_{tt}(K_{ac}, K_{bd})$ is most complex. These coefficients are related to one another by the simple expression

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_a, K_b) = \sum_d \gamma_{ac}\gamma_{bd}N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ac}, K_{bd})\,s_{cd}, \quad (43)$$

which is fulfilled for any $c \neq a$. The following equation, analogous to Eqn. (43),

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ac}, K_{bd}) = \sum_f \gamma_{ace}\gamma_{bdf}N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ace}, K_{bdf})\,s_{ef}, \quad (44)$$

is fulfilled for any $e \neq a, c$. The symbol $\gamma_{abc} = (1-\delta_{ab})(1-\delta_{ac})(1-\delta_{bc})$. The quantities $N^{[\lambda]}_{tt}(K_{ace}, K_{bfd})$ are determined from equations analogous to Eqns. (38) and (40):

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ace}, K_{bdf}) = \sum_{P''}\Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P''P^{i_a i_c i_e}_{bdf})\langle\Phi_0(K_{ace})|P''\Phi_0(K_{bdf})\rangle. \quad (45)$$

Analogous quantities can be determined for the configuration with four "separated" orbitals, etc., including the limiting case corresponding to the "separation" of all N orbitals of the configuration:

$$N^{[\lambda]}_{\bar{t}\bar{t}}(K_{ace\ldots q}, K_{bdf\ldots r}) = \Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P^{i_a i_c i_e \ldots i_q}_{bdf\ldots r}). \quad (46)$$

It is convenient to use the chain of recurrence equations (43)–(46) for the computer calculation of $N^{[\lambda]}_{tt}$. For this it is sufficient to give the matrix of the overlap integrals and the matrices of the transpositions $\Gamma^{[\lambda]}(P_{i,i+1})$, since all other permutations are expressed in terms of the products of transpositions of this type. Here it is necessary to take account of the fact that the form of the coefficients $N^{[\lambda]}_{tt}$ remains unchanged for identical permutations of the indices in the two configurations appearing in the argument.

In the case of a configuration of orthogonal orbitals, the expressions for the matrix elements are simplified considerably. An arbitrary configuration of orthogonal orbitals

$$K: \varphi_a^{n_a}\varphi_b^{n_b}\ldots\varphi_q^{n_q},\ \sum_a n_a = N,\ \langle\varphi_a|\varphi_b\rangle = \delta_{ab}. \quad (47)$$

can be considered. Expressions can be obtained for the matrix elements, diagonal with respect to configuration, of the operators F and G. The matrix element of the operator F is independent of the symmetry of the state

$$\langle Kt|F|K\bar{t}\rangle^{[\lambda]} = \delta_{\bar{t}\bar{t}}\sum_a n_a f_{aa}. \quad (48)$$

For the operator G, an elegant result is obtained: the entire dependence on spin is included in the coefficient of the exchange integral:

$$\langle Kt|G|K\bar{t}\rangle^{[\lambda]} = \delta^{t}_{\bar{t}\bar{t}}\sum_a{}' g_{aa,aa} + \sum_{a<b} n_a n_b\,[\delta_{\bar{t}\bar{t}}g_{ab,ab} + \Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P_{ab})\,g_{ab,ba}]. \quad (49)$$

The prime of the sum over a denotes that the sum is taken only over doubly-filled orbitals. The coefficients of the exchange integrals are equal to the matrix elements of the transposition P_{ab} between the orbitals. If the orbitals φ_a and φ_b are doubly filled, it is possible to take as P_{ab} any permutation of the electrons between the orbitals φ_a and φ_b, since for these permutations, $\Gamma^{[\lambda]}_{tt}(P_{ab})$ are identical.

For brevity, the following symbols are introduced:

$$g_{ab,ab} = \alpha_{ab},\ g_{ab,ba} = \beta_{ab}.$$

Eqns. (48) and (49) make it possible to represent the matrix elements of the Hamiltonian $\mathcal{H} = F + G$ as a sum of two terms. The first contains the one-electron and Coulomb integrals, and the second is the sum of only exchange integrals:

$$\langle Kt|\mathcal{H}|Kt\rangle^{[\lambda]} = \delta_{\bar{t}\bar{t}}Q + J^{[\lambda]}_{\bar{t}\bar{t}}, \quad (50)$$

where

$$Q = \sum_a n_a f_{aa} + \sum_a{}'\alpha_{aa} + \sum_{a<b} n_a n_b \alpha_{ab}, \quad (51)$$

$$J^{[\lambda]}_{\bar{t}\bar{t}} = \sum_{a<b} n_a n_b \Gamma^{[\lambda]}_{\bar{t}\bar{t}}(P_{ab})\,\beta_{ab}. \quad (52)$$

The non-diagonal elements of the energy matrix contain only the exchange integrals with coefficients which depend on the spin of the state. Since a contribution to the spin is made only by unpaired electrons, the coefficients of the exchange integrals can be determined in the group of the permutations of not all but only the unpaired electrons. For this purpose, the configuration K must be represented in the form K_0K_1, putting the doubly filled orbitals first (configuration K_0), and then the singly filled orbitals (configuration K_1). The Young diagram characterising the symmetry of the configuration K_1 is obtained from the Young diagram $[\lambda]$ by removing the m upper rows (m is the number of doubly filled orbitals), and is denoted $[\lambda^{(m)}]$. In the equation given below, the letters a and b are used to denote the orbitals of the configuration K_0 and the letters c and d the orbitals of the configuration K_1. Thus by making use of the properties of the standard representation of the group of permutations[14] for the spin-dependent non-diagonal elements of the Hamiltonian (52), it is possible to obtain the following expression:

$$J^{[\lambda]}_{\bar{t}\bar{t}} = -\sum_{a<b} 2\beta_{ab} - \sum_{a,c}\beta_{ac} + \sum_{c<d}\Gamma^{[\lambda^m]}_{t_i t_i}(P_{cd})\,\beta_{cd}. \quad (53)$$

In molecular calculations, the number of singly filled molecular orbitals is usually small. The matrices $\Gamma^{[\lambda]}(P_{ab})$ for all transpositions of the groups π_3–π_4 and the transpositions of the type $P_{i,i+1}$ of the groups π_5–π_6 are given in the Appendix to Ref. 14, and the matrices of all the transpositions of the groups π_3–π_6 are given in the expanded edition of the book by the present author[46].

VII. SPIN-PROJECTED SELF-CONSISTENT FIELD EQUATIONS

In the valence bond method and in the simple molecular orbital method, the one-electron functions are assumed to be known. It is possible, however, in the one-particle approximation, to formulate the many-electron problem without imposing previous restrictions on the one-electron functions. This approach, first proposed and developed for the atom by Hartree[47] and Fock[48] (see also Slater's paper[49]), is usually called the Hartree–Fock or self-consistent field (SCF) method.

The derivation of the equations which must be satisfied by the one-electron functions being sought is based on the variation principle

$$\bar{E} = \int \Psi^* \mathcal{H} \Psi \, \mathrm{d}V = \min \tag{54}$$

with the additional condition

$$\int \Psi^* \Psi \, \mathrm{d}V = 1, \tag{55}$$

but only the determinants of the one-electron functions are allowed as competing functions. Since for arbitrary Ψ the variation principle (54) and (55) leads to the Schrödinger equation (see for example Ref. 19), the best function of this type is found by solving the variation problem with a determinantal wavefunction.

In molecular calculations, the term Hartree–Fock equation is usually employed to describe the SCF equations obtained in the description of the system by a single determinant with doubly filled orbitals. This determinant corresponds to the spin $S = 0$, and describes the ground state of most molecules. The derivation of the Hartree–Fock equations can also be carried out without relating it to the determinantal representation of the wavefunction. As noted above, all the properties of a molecule which are independent of spin interactions are described by giving only the coordinate wavefunction. In fact, the derivation of the SCF equations requires only an expression for the average value of the energy in the state being considered. By partitioning the total wavefunction into coordinate and spin functions, expressions of this kind were obtained in the previous section for an arbitrary configuration in a state with a definite value of the spin S. This makes it possible to derive the SCF equations in the general case and to obtain all particular cases from them, without deriving these equations separately for each state being considered, as has to be done when operating with wavefunctions in the form of linear combinations of determinants.

With allowance for Eqns. (48) and (49), an expression can be written for the average energy in a form symmetrical with respect to the indices a and b:

$$\bar{E} = \mathcal{H}_{tt}^{[\lambda]}(K) = \sum_a n_a f_{aa} + \frac{1}{2}\sum_{a,b} \beta(n_a, n_b)\,[\alpha_{ab} + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\beta_{ab}],$$
$$\beta(n_a, n_b) = \begin{cases} n_a n_b & a \neq b, \\ 1 & a = b. \end{cases} \tag{56}$$

For $a = b$, $\Gamma_{tt}^{[\lambda]}(P_{ab}) = 1$. Following Roothaan[50], it is possible to introduce Coulomb $\hat{\alpha}_b$ and exchange $\hat{\beta}_b$ operators, defined by the relationships

$$\hat{\alpha}_b(i)\,\varphi_a(i) = \left[\int \varphi_b^*(j)\,\varphi_b(j)\,g_{ij}\,\mathrm{d}V_j\right]\varphi_a(i),$$
$$\hat{\beta}_b(i)\,\varphi_a(i) = \left[\int \varphi_b^*(j)\,\varphi_a(j)\,g_{ij}\,\mathrm{d}V_j\right]\varphi_b(i). \tag{57}$$

It can readily be verified that the operators $\hat{\alpha}_b$ and $\hat{\beta}_b$ are Hermitian, that is they satisfy the relationships§

$$\langle\psi|\hat{\alpha}_b|\varphi\rangle = \langle\varphi^*|\hat{\alpha}_b^*|\psi^*\rangle,$$
$$\langle\psi|\hat{\beta}_b|\varphi\rangle = \langle\varphi^*|\hat{\beta}_b^*|\psi^*\rangle. \tag{58}$$

The operators (57) make it possible to write the Coulomb and exchange integrals as one-electron integrals:

$$\alpha_{ab} = \langle\varphi_a|\hat{\alpha}_b|\varphi_a\rangle = \langle\varphi_b|\hat{\alpha}_a|\varphi_b\rangle,$$
$$\beta_{ab} = \langle\varphi_a|\hat{\beta}_b|\varphi_a\rangle = \langle\varphi_b|\hat{\beta}_a|\varphi_b\rangle. \tag{59}$$

The following expression is obtained for the average energy E (56) with allowance for Eqns. (59):

$$\bar{E} = \sum n_a\langle\varphi_a|\hat{f}|\varphi_a\rangle + \frac{1}{2}\sum_{a,b}\beta(n_a, n_b)\langle\varphi_a|\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b|\varphi_a\rangle. \tag{60}$$

Thus the solution of the variation problem (54) and (55) involves the determination of the set of orbitals φ_a minimising the energy (60), with fulfilment of the conditions for orthonormalisation of the orbitals

$$\langle\varphi_a|\varphi_b\rangle = \delta_{ab}. \tag{61}$$

This problem can be solved by the Lagrange method, and reduces to the determination of the unconditional extremal value of the function

$$J = \sum_a \left\langle \varphi_a \left| n_a\hat{f} + \frac{1}{2}\sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b \right| \varphi_a \right\rangle - \sum_{ab}\varepsilon_{ba}\langle\varphi_a|\varphi_b\rangle, \tag{62}$$

where ϵ_{ab} represents the Lagrange factors. For this it is necessary to find the first variation of the functional J. When taking the variation with respect to φ_b^* and φ_b, it is convenient to use the equivalence of the two forms in which the Coulomb and exchange integrals (59) can be written. Allowance for the Hermitian character of the operators $\hat{f}$, $\hat{\alpha}_b$, and $\hat{\beta}_b$ makes it possible to represent the variation in the form

$$\delta J = \sum_a \left\langle \delta\varphi_a \left| n_a\hat{f} + \sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b] \right| \varphi_a \right\rangle - \sum_{a,b}\langle\delta\varphi_a|\varepsilon_{ba}\varphi_b\rangle +$$
$$+ \sum_a \left\langle \delta\varphi_a^* \left| n_a\hat{f} + \sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b^* + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b^*] \right| \varphi_a^* \right\rangle - \sum_{a,b}\langle\delta\varphi_a^*|\varepsilon_{ab}\varphi_b^*\rangle. \tag{63}$$

By equating δJ to zero and making allowance for the independence of the variations $\delta\varphi_a$ and $\delta\varphi_a^*$, it is possible to obtain two complex-conjugate systems of equations, which are equivalent if the matrix of the Lagrange coefficients is Hermitian:

$$\varepsilon_{ba} = \varepsilon_{ab}^*. \tag{64}$$

The required set of minimising orbitals should be a solution of the integro-differential equations

$$\hat{\mathcal{H}}_a\varphi_a = \sum_b \varepsilon_{ba}\varphi_b, \quad a = 1, 2, \ldots N - m \tag{65}$$

with the one-electron Hamiltonian

$$\hat{\mathcal{H}}_a = n_a\hat{f} + \sum_b \beta(n_a, n_b)\,[\hat{\alpha}_b + \Gamma_{tt}^{[\lambda]}(P_{ab})\,\hat{\beta}_b]. \tag{66}$$

The system of $(N - m)$ equations (65) and (66) contains $(N - m)$ unknown functions φ_a (for the configuration of singly filled orbitals there are N functions, and for the configuration K_0 with all doubly filled orbitals there are $N/2$ functions) and $(N - m)^2$ unknown Lagrange factors ϵ_{ba}.

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§ It may be remembered that $\langle\psi|\hat{\alpha}_b|\varphi\rangle \equiv \int\psi^*\hat{\alpha}_b\varphi\,\mathrm{d}V$.

It must therefore be supplemented by an additional $(N-m)^2$ equations. Multiplication of Eqn. (65) by φ_b^* and integration with respect to the whole of space give

$$\varepsilon_{ba} = \langle \varphi_b | \hat{\mathcal{H}}_a | \varphi_a \rangle. \quad (67)$$

In practice, it is more convenient to use the more symmetrical form of writing the Lagrange factors:

$$\varepsilon_{ba} = \frac{1}{2}\langle \varphi_b | \hat{\mathcal{H}}_a + \hat{\mathcal{H}}_b | \varphi_a \rangle. \quad (68)$$

Eqns. (65) describe the state of an arbitrary molecular configuration with value of the total spin S. In this general case, each orbital φ_a has its own Hamiltonian $\hat{\mathcal{H}}_a$; the coefficients ϵ_{ba} do not have a definite physical significance.

For a closed electron level, when all the orbitals are doubly filled, Eqns. (65) are simplified. This state corresponds to the spin $S = 0$, and the orbital Young diagram $[\lambda] = [2^m]$. Since $\Gamma^{[2n]}(P_{ab}) = -1/2$ (see Ref. 14), $n_a = n_b = 2$, and $\hat{\alpha}_b$ and $\hat{\beta}_b$ are equivalent for $a = b$, it is found that all orbitals of the configuration K_0 satisfy the single equation

$$\hat{\mathcal{H}}_0 \varphi_a = \sum_b \varepsilon_{ba} \varphi_b, \quad (69)$$

$$\hat{\mathcal{H}}_0 = 2\hat{f} + 2\sum_b (2\hat{\alpha}_b - \hat{\beta}_b). \quad (70)$$

It can readily be shown (see Ref. 50) that the operator (70) is invariant with respect to an arbitrary unitary transformation of the orbitals. If the transformation which diagonalises the Hermitian matrix of the Lagrange factors (68) is used as unitary transformation, Eqns. (69) can be transformed to a problem in the eigenvalues of the operator $\hat{\mathcal{H}}_0$.

$$\hat{\mathcal{H}}_0 \varphi_a = 2\varepsilon_a \varphi_a. \quad (71)$$

The factor 2 in front of ϵ_a is introduced so that ϵ_a has the significance of the energy of the electron in the orbital φ_a¶. By separating the analogous factor from the operator $\hat{\ }_0$ (70), it is possible to obtain the familiar Hartree–Fock equation for a closed level

$$\hat{\mathcal{H}}_0 \varphi_a = \varepsilon_a \varphi_a, \quad (72)$$

$$\hat{\mathcal{H}}_0 = \hat{f} + \sum_b (2\hat{\alpha}_b - \hat{\beta}_b). \quad (73)$$

The orbitals satisfying the Hartree–Fock equations (72) are eigenfunctions of the same Hamiltonian. From this it follows immediately that: a) the self-consistent orbitals corresponding to different eigenvalues of Eqn. (72) are orthogonal to one another; and b) the orbitals corresponding to a given eigenvalue transform as the irreducible representations of the symmetry group of the Hamiltonian (if there is no accidental degeneracy). The operator $\hat{\mathcal{H}}_0$ consists of the one-electron operator $\hat{f}$, the symmetry of which is determined by the equilibrium configuration of the nuclei, that is it coincides with the symmetry group of the molecule, and the sum of the Coulomb and exchange operators, which depends on the orbitals. The last sum, as noted above, is scalar with respect to the operations of the unitary group, and hence to the operations of its point sub-group. Thus the symmetry of the Hamiltonian coincides with the symmetry of the operator $\hat{f}$, and the solutions of the Hartree–Fock equation should transform as the irreducible representations of the symmetry point group of the molecule.

It is obvious that

$$\varepsilon_a = \langle \varphi_a | \mathcal{H}_0 | \varphi_a \rangle = f_{aa} + \sum_b (2\alpha_{ab} - \beta_{ab}). \quad (74)$$

If the sum of the energies ϵ_a over all electrons, is now taken, it is found that

$$2\sum_a \varepsilon_a = 2\sum_a f_{aa} + 2\sum_{a,b} (2\alpha_{ab} - \beta_{ab}). \quad (75)$$

On the other hand, the total energy of the electrons for the configuration K_0 being considered, according to Eqn. (50), is

$$E_0 = 2\sum_a f_{aa} + \sum_{a,b} (2\alpha_{ab} - \beta_{ab}), \quad (76)$$

that is the sum of the one-electron energies is greater than the total energy of this system by an amount corresponding to the energy of interaction of the electrons. This is related to the fact that in the summation with respect to all the electrons, the interaction of each pair of electrons was included twice. It may be noted that it is because the total energy is not equal to the sum of the one-electron energies that the filling of the orbital states does not always take place in order of increasing ϵ_a, since the term containing the interaction

$$\sum_{a,b} (2\alpha_{ab} - \beta_{ab})$$

may compensate the loss in energy, obtained by the "irregular" filling of the orbitals.

The expression for the total energy (76) can also be written in the additive form:

$$E_0 = \sum_a \left(2f_{aa} + \sum_b (2\alpha_{ab} - \beta_{ab})\right) = \sum_a \varepsilon'_a, \quad (77)$$

$$\varepsilon'_a = 2\varepsilon_a - \sum_b (2\alpha_{ab} - \beta_{ab}), \quad (78)$$

that is the electronic energy can be represented as the sum of appropriately renormalised one-electron energies. This explains why, with an appropriate selection of parameters in some semi-empirical calculations, it is possible not to take explicit account of electron interactions (for example in the Hückel method).

VIII. THE USE OF THE APPARATUS OF CONTINUOUS GROUPS IN QUANTUM-CHEMICAL CALCULATIONS

The mathematical apparatus of unitary groups can be used not only for the classification of states[38–41,51] but also directly in the calculation of the matrix of the Hamiltonian[6–9,59,60]. Its application is based on the following features.

A many-electron wavefunction can always be expanded in a series with respect to products of orthonormalised one-electron functions (spin-orbitals). This expansion is accurate when account is taken of all configurations in the complete (infinite) set of one-electron functions. Practical

¶ The need to introduce the factor 2 for the interpretation of φ_a as the one-electron energy is related to the fact that when taking account of the bonding conditions by means of the Lagrange factor in Eqn. (62), the summation was carried out only with respect to the orbitals, without allowance for the multiplicity of the filling. Thus in the SCF equations, represented in the form of the eigenvalue problem of the one-electron operator $\mathcal{H}_a(i)$, ϵ_a characterises the total energy of all the electrons in the orbital φ_a, that is, for doubly filled orbitals, the energy of two electrons.

calculations are naturally based on a finite set; its order is denoted $2q$. These $2q$ orthonormalised spin-orbitals can be regarded as the basis unit vectors of a $2q$-dimensional vector space. The complete many-electron wavefunction is constructed from the products of N vectors of this space, and is an antisymmetric tensor of rank N in the space of $2q$ measurements. In the original one-electron basis it is possible to construct a model Hamiltonian for which a given many-electron function is not an approximate but an exact eigenfunction. In the representation of secondary quantisation, the model Hamiltonian has the following form:

$$\mathcal{H} = \sum_{k,l}^{2q} f_{kl} a_k^+ a_l + \frac{1}{2} \sum_{kl,m,n} g_{km,ln} a_k^+ a_m^+ a_n a_l, \qquad (79)$$

where the operators for the generation a_k^+ and annihilation a_k of an electron in the state $k = \varphi_a \chi \sigma_k$ satisfy the fermion commutation relationships:

$$[a_k, a_l^+]_+ = \delta_{kl}, \quad [a_k^+, a_l^+]_+ = [a_k, a_l]_+ = 0. \qquad (80)$$

For the operators f_i and g_{ij}, which do not depend on spin, the matrix elements are

$$f_{kl} = \delta_{\sigma_k \sigma_l} f_{ab}, \quad g_{km,ln} = \delta_{\sigma_k \sigma_l} \delta_{\sigma_m \sigma_n} g_{ab,cd}, \qquad (81)$$

when the one-electron and two-electron matrix elements f_{ab} and $g_{ab,cd}$ are defined in the orbitals φ_a, and not in the spin-orbitals k.

If the matrix elements (81) are not calculated, but are found from the comparison with experimental data, Eqn. (79) is a semi-empirical model Hamiltonian. Thus in the Pariser–Parr–Pople Hamiltonian

$$g_{ab,cd} = \delta_{ac} \delta_{bd} I_{ab}, \qquad (82)$$

and in the Hubbard Hamiltonian

$$g_{ab,cd} = \delta_{ac} \delta_{bd} \delta_{ab} I. \qquad (83)$$

Using the anticommutation relationships (80), it can readily be shown that the commutator

$$[a_k^+ a_l, a_m^+ a_n]_- = \delta_{lm} a_k^+ a_n - \delta_{kn} a_m^+ a_l. \qquad (84)$$

Eqns. (84) coincide with the commutation relationships for the infinitesimal generators of the unitary group, defining the structural constants of the corresponding Lie algebra[6,17]:

$$[E_{kl}, E_{mn}]_- = \delta_{lm} E_{kn} - \delta_{kn} E_{ml}. \qquad (85)$$

Thus the operators a_k^+ and a_l are algebraically equivalent to the infinitesimal generators E_{kl} of the unitary group, and can be identified with them.

Since

$$a_k^+ a_m^+ a_n a_l = a_k^+ a_l a_m^+ a_n - \delta_{lm} a_k^+ a_n, \qquad (86)$$

the Hamiltonian (79) can be expressed in terms of the generators E_{kl}. Thus

$$\mathcal{H} = \sum_{k,l}^{2q} f_{kl} E_{kl} + \frac{1}{2} \sum_{k,l,m,n} g_{km,ln} [E_{kl} E_{mn} - \delta_{lm} E_{kn}]. \qquad (87)$$

As noted above, a many-electron wavefunction is an antisymmetric tensor of rank N in the space of $2q$ measurements. Since the Hamiltonian is assumed to be independent of the spin variables, the total wavefunction can be broken down into coordinate and spin functions, and the coordinate wavefunction is defined in the space of q measurements. For unitary transformations of space, the coordinate wavefunction transforms as the tensor representation of the group U_q. The representation breaks down into the irreducible representations $U_q^{[\lambda]}$ on symmetrisation of the tensor in accordance with a Young diagram of N squares[14,52]. As early as 1950, Gel'fand and Tseitlin[53,54] determined the canonical basis for the irreducible representations of the unitary group, in which there are simple equations for the matrix elements of the infinitesimal generators of the unitary group, Since the Hamiltonian (87) is a polynomial of second degree in the generators E_{kl}, the problem of calculating the matrix elements using the Gel'fand–Tseitlin basis becomes very simple.

A similar approach was proposed by Matsen[6], and realised by Paldus[8] for computer calculation in the approximation of the configuration interaction method. The program compiled is very efficient. Thus for a six-electron problem and the Pariser–Parr–Pople Hamiltonian, the time required on an IBM 360/75 computer for calculating the complete matrix of the configuration interaction for singlet states (order of the matrix 175×175) or triplet states (order of the matrix 198×198) is less than 1 s.[8]

The use of an anlogous approach for calculating atomic states was proposed by Patera[55] and Harter[9,56]. In a central field for an orbital momentum of the electron $l \geq 2$, the problem of the additional quantum numbers identifying the state arises, since the same value of the total orbital momentum L may be encountered several times in a configuration[14,57]. For the one-level configuration l^N, the space of the orthogonal orbitals has the dimension $2l + 1$. In unitary transformations of this space, the many-electron coordinate function transforms as the tensor representation of the group of unitary transformations U_{2l+1}. The Gel'fand–Tseitlin basis separates the irreducible representations $U_{2l+1}^{[\lambda]}$ and corresponds to the reduction in the chain of groups $U_{2l+1} \subset U_{2l} \supset U_{2l-1} \supset \ldots \supset U_1$. This reduction ensures that a complete set of quantum numbers is obtained for all many-electron states.

However, although the wavefunctions in the Gel'fand–Tseitlin basis are eigenfunctions of the operators $\hat{S}^2$, $\hat{S}_Z$, and L_Z, they do not correspond to a definite value of the orbital momentum L. This leads to large orders of the secular equations. This is not a problem for modern fast computers, but for carrying out analytical calculations, the generally accepted procedure for calculations using the Racah technique appears much more convenient. There therefore does not seem to be sufficient basis for the opinion, put forward by Harter and Patterson[9], that the method of calculation using the apparatus of unitary groups should completely replace the Racah method. A more detailed comparison of the two methods is given in a review[58] of the book by Harter and Patterson[9].

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Diazenium Salts

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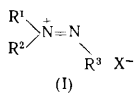
The literature on compounds of the type $[R^1R^2N=NR^3]^+X^-$ (diazenium salts) is surveyed. Their structures and properties are considered and methods for their synthesis as well as a wide variety of the chemical reactions of these reactive hydrazine derivatives are discussed.
The bibliography includes 122 references.

CONTENTS

I. Introduction 563
II. Methods of preparation 563
III. Structure and spectroscopic characteristics 566
IV. The acid properties of diazenium cations 568
V. Reactions of diazenium salts 570

I. INTRODUCTION

Diazenium salts constitute a new class of nitrogen compounds having the general formula (I) containing the functional group $\rangle N^+=N$, which is not part of an aromatic system:



(I)

R^1=H, Alk, or Ar;
R^2=H, Alk, or Ar;
R^3=H, Alk, Ar, OAlk, or OAc;
X^-=Hal^-, ClO_4^-, BF_4^-, $SbCl_6^-$, etc.

The cations of diazenium salts are referred to as diazenium cations. The name of the salts is based on the nomenclature proposed for compounds containing two adjacent nitrogen atoms[1]. The complete name indicates the anion and all the substituents and their positions in the cation. For example, $[Me_2N^+=NH]Br^-$ is 1,1-dimethyldiazenium bromide, $[(PhCH_2)_2N^+=NOEt]BF_4^-$ is 1,1-dibenzyl-2-ethoxydiazenium tetrafluoroborate, and $[Ph_2N^+=NPh]ClO_4^-$ is triphenyldiazenium perchlorate.

The closest analogues of diazenium salts are, on the one hand, the well known diazonium salts and, on the other hand, the immonium salts $[R_2N^+=CR'_2]X^-$; one may therefore expect some similarity between the structures and properties of these compounds, which, as will be shown below, is indeed the case. The behaviour of diazenium salts is fully determined by the structure of the cation; the nature of the anion is not very important. Diazenium salts can be divided into several groups on the basis of the number and nature of substituents in the cation, differing appreciably in stability, properties, and the extent to which they have been investigated.

1,1-Disubstituted salts (I, R^3 = H), which have attracted the attention of investigators for a number of reasons, have been studied in greatest detail. Firstly, they are of interest in connection with the study of the mechanism of the oxidation of 1,1-disubstituted hydrazines, which is of practical importance; in acidic media this process proceeds via a stage involving the formation of the corresponding diazenium cations and the properties of the latter in many respects determine further reactions. Secondly, 1,1-disubstituted diazenium cations can be regarded as the conjugate acids of 1,1-diazenes or aminonitrenes $[R_2N^+=\bar{N} \rightleftharpoons R_2N-\ddot{N}:]$, which are unstable sextet species playing an important role in the chemistry of hydrazine derivatives[2-4]. The relation between aminonitrenes and 1,1-disubstituted diazenium cations, their interconversions in the reactions of hydrazine derivatives, and the possibility of regenerating aminonitrenes from 1,1-disubstituted diazenium salts are therefore of interest. Finally, many reactions of these salts are of independent synthetic value.

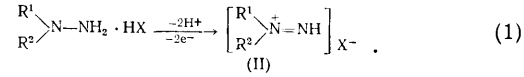
On the other hand, the properties of the isomeric 1,2-disubstituted diazenium salts have been scarcely investigated. There is also little information about the trisubstituted salts, with the exception of the so-called alkoxydiazenium salts (I, R^3 = OAlk). Fully unsubstituted and monosubstituted diazenium salts are so far unknown. The corresponding cations are apparently extremely unstable and, even if they can be generated in some reactions, so far no one has been able to detect their formation.

The literature dealing with diazenium salts is extensive, but hitherto has not been treated systematically to any great extent. Previously the syntheses and properties of diazenium salts were partly dealt with in reviews of aminonitrenes[2,3] and also in a review of reactive nitrogen-containing intermediates[5], but, in our opinion, their treatment has been inadequate. Furthermore, in recent years many new important studies have been published in this field. It therefore appears necessary to describe the present state of the chemistry of diazenium salts.

II. METHODS OF PREPARATION

1. Oxidation of Hydrazine Derivatives

In 1957 McBride[6] established that, whereas the oxidation of the simplest 1,1-dialkylhydrazines in an alkaline or neutral medium (a reaction known since the time of E. Fischer) leads to 2-tetrazenes, in an acidic medium in the cold the products obtained after the consumption of two equivalents of the oxidants are previously unknown compounds whose spectroscopic and chemical properties correspond to the structure of "diazo-like substances" (II):



(1)

(II)

McBride regarded the cations in (II) as protonated aminonitrenes (1,1-diazenes)[2-5] and therefore subsequently proposed[7] that they be called 1,1-disubstituted diazenium cations and that the salts (II) be referred to as diazenium salts.

Since then the oxidation of asymmetric disubstituted hydrazines in an acid medium [Eqn.(1)] became the usual and virtually the only method of synthesising 1,1-disubstituted diazenium salts. The oxidants used for 1,1-dialkylhydrazines have usually been halogens and alkali metal halogenates.[6-25] In addition, use was made of transition metal salts [Ce(IV) [25], Hg(II),[26] Cu(II) [27]] and peracids.[28] Hünig postulated the formation of diazenium cations in the oxidation of a number of 1,1-diarylhydrazines by $FeCl_3$ and $K_3[Fe(CN)_6]$.[29,30] However, in the latter case the oxidation was carried out in a weakly acidic (CH_3COOH) and even alkaline (pyridine, ammonia) media; under these conditions, 1,1-disubstituted diazenium salts cannot exist for any long period (see below); Hünig's claim therefore appears doubtful. It has been reported[14] that the oxidation of arylhydrazines with bromine yielded only decomposition products. However, it is more likely that this process involves the usual bromination of the aromatic ring, analogous to the bromination of analines, rather than oxidation, and that diazenium salts are not formed at all. Chemical oxidation has usually been carried out in aqueous solutions and only once in acetonitrile.[14]

Diazenium salts have been obtained by the electrochemical oxidation of 1,1-diaryl- and 1-alkyl-1-arylhydrazines at platinum electrodes in acetonitrile[14,31-37] and also of 1,1-dimethylhydrazine in aqueous H_2SO_4.[25,38] However, the attempt at an anodic oxidation of 1,1-dimethylhydrazine to a diazenium salt in acetonitrile under conditions completely identical with those in the oxidation of arylhydrazines was unsuccessful: oxidation does not occur in the presence of acid and in neutral and alkaline media other products are formed[39]. Nor was it possible to oxidise 1,1-dibenzylhydrazine under these conditions[14].

It follows from coulometric data[31-34,36-38,40,41] and from the results of potentiometric titration of 1,1-disubstituted hydrazines with KIO_3 in acid solutions[42] that two-electron oxidation takes place in conformity with Eqn.(1), the products being comparatively stable species which are not oxidised further. The EPR spectrum recorded in the oxidation of 1,1-dimethylhydrazine by Ge(IV) in H_2SO_4 showed the presence of the signal of the 1,1-dimethylhydrazinium radical-cation $[(CH_3)_2NNH_2]^{\cdot+}$, which led to the conclusion that the oxidation of 1,1-disubstituted hydrazines in acid solutions (at least by one-electron oxidants) proceeds in two stages and that the diazenium cation is preceded by the hydrazinium radical-cation[25]. On the other hand, in the electrochemical oxidation of the same hydrazine there are no EPR signals. In this case hydrazine apparently loses both electrons almost simultaneously at the anode surface[25].

The 1,1-disubstituted diazenium salts formed in the oxidation process in almost quantitative yields are most stable in strongly acidic solutions below 5°C, but even under these conditions they decompose slowly, the rate of decomposition increasing with temperature[6]. Salts with aryl substituents are stable only in non-aqueous solutions.

A salt of type (II) has been synthesised in a dry form in only one instance—McBride obtained crystalline 1,1-dimethyldiazenium perchlorate[6]:

$$Me_2NNH_2 + I_2 + 2AgClO_4 \rightarrow [Me_2\overset{+}{N}{=}NH]\,ClO_4^- + HClO_4 + 2AgI\ .$$

It is noteworthy that the fully stable hydrazides of sulphonic acids (III) can be regarded formally as diazenium salts. It is claimed that in both acid[17] and neutral and alkaline polar solutions[43] they can dissociate reversibly into diazenium cations and sulphinate anions:

$$\underset{\text{(III)}}{R^1R^2N{-}NHSO_2R^3} \rightleftharpoons \left[R^1R^2\overset{+}{N}{=}NH\right] + R^3SO_2^- \quad (2)$$

The occurrence of this equilibrium has been confirmed by a number of experiments on the exchange of sulphonic acid residues in hydrazides[43] (see Section V in this review), from which it follows, in particular, that 1,1-dialkylhydrazides dissociate most readily. However, even for these substances the position of equilibrium (2) is apparently strongly displaced to the left, since signals corresponding to diazenium cations could not be detected in the ^1H NMR spectra of their solutions[43]. The dissociation itself can be regarded as an intramolecular oxidation-reduction process: here the hydrazinium residue is oxidised to the diazenium cation and the sulphonyl group is reduced to the sulphinate ion.

Trisubstituted salts (I, R^3 = Ar or t-Bu) can be obtained by the chemical (Ag^+)[44] and electrochemical[34,37,44-46] oxidation of the corresponding trisubstituted hydrazines, which is in many ways analogous to the formation of 1,1-disubstituted diazenium salts:

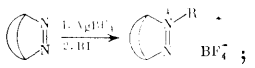
$$R^1R^2N{-}NHR^3 \xrightarrow[-H^+,-2e^-]{X^-} R^1R^2\overset{+}{N}{=}NR^3\ X^-\ . \quad (3)$$

However, the anodic oxidation of trimethylhydrazine in acetonitrile does not occur in the presence of acid, while in neutral and alkaline media formaldehyde dimethylhydrazone is formed[39]. At the same time, it is believed that the chemical oxidation of trimethylhydrazine in aqueous acid solutions and the dissociation of 1,1,2-trimethyl-2-tosylhydrazine,[17] analogous to the reaction (2), proceed via the formation of the trimethyldiazenium cation. Other trisubstituted hydrazines, which have no dissociable protons at the α-carbon atoms of the substituents, can be oxidised electrochemically in neutral and alkaline media to the corresponding diazenium cation; however, on being protonated, they are not oxidised even in aqueous solutions[44].

2. The Alkylation of Azo-Compounds and *N*-Nitrosamines

Apart from the anodic oxidation of trisubstituted hydrazines, treatment of azo-compounds with strong alkylating agents constitutes an effective method for the synthesis of trisubstituted diazenium salts. Dry crystalline salts, which are fairly stable in air, are obtained in 60–90% yield.

Thus 2,3-diazabicyclo[2,2,1]heptane and a number of azo-compounds with a symmetrical environment around the azo-group have been alkylated[44,47,48]:



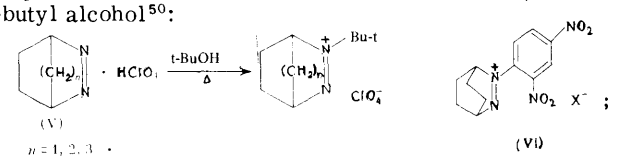
R = Me, Et, or t-Bu;

a series of 1,2-diaryl-1-methyldiazenium salts have been obtained[49]:

$$\underset{\substack{\text{(IV)}\\ R = F \text{ or } CF_3.}}{ArN{=}NAr'} \xrightarrow{MeOSO_2R} \underset{RSO_3^-}{\overset{Ar}{\underset{Me}{\overset{+}{N}}}{=}NAr'} + \underset{RSO_3^-}{ArN{=}\overset{+}{N}\overset{Ar'}{\underset{Me}{<}}}\ ;$$

If Ar = Ar′ in (IV), then alkylation proceeds preferentially and sometimes exclusively at the nitrogen atom linked to the more electron-donating substituent. When the ring contains an electron-accepting substituent, the nitrogen atom linked to it is not alkylated[49].

Trisubstituted diazenium salts are obtained unexpectedly readily and smoothly (85–90% yield) by refluxing the perchlorates of bicyclic azo-compounds (IV), in t-butyl alcohol[50]:



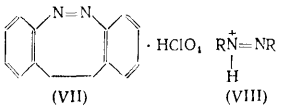
(V)

$n = 1, 2, 3$.

(VI)

It is remarkable that in all the instances described the introduction of the t-butyl group into the molecule does not entail the liberation of isobutene.[44] Under still milder conditions (25°C, ether), the salt (VI, X = Br) can be obtained in 83% yield from 2,3-diazabicyclo[2,2,2]octene and 1-bromo-2,4-dinitrobenzene.[50]

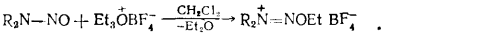
The alkylation of protonated azo-compounds proceeds similarly[50–52]. It follows from the ^{1}H NMR spectra of certain azo-compounds in strongly acid media at a low temperature[51,52] and also from electronic spectroscopy for chemical analysis (ESCA) that the protonation of both the *cis*- and *trans*-forms of azobenzene, pyridazine, and *o*,*o'*-azobibenzyl (VII) [52] gives rise to asymmetric classical ions (VIII):



(VII) (VIII)

i.e. 1,2-disubstituted diazenium cations are produced and not a bridge ion with the proton located symmetrically relative to both nitrogen atoms. Many facts, previously treated as evidence for the formation of non-classical ions and which have aroused a prolonged discussion concerning the structure of protonated azo-compounds (see Refs. 51 and 52 and the literature quoted therein), can apparently be accounted for by very rapid proton transfer between two nitrogen atoms under the usual conditions, for example, in solutions. The classical structure of protonated azo-compounds is supported by the fact that, according to calculations in terms of CNDO/2 and MINDO/2 approximations for protonated azomethane and azobenzene, the ion (VIII) is more stable than any of the possible bridge ions[52]. Thus the salts of azo-compounds can be regarded as 1,2-disubstituted diazenium salts.

In 1962 Hünig and coworkers obtained alkoxydiazenium salts for the first time by the reaction of aliphatic *N*-nitrosamines with triethyloxonium tetrafluoroborate [53]:

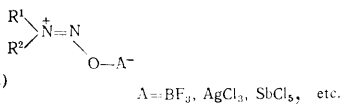


Since then alkoxydiazenium salts have been obtained by the alkylation of purely aliphatic and alkylaryl-substituted *N*-nitrosamines with trialkyloxonium tetrafluoroborates,[53–57] trialkyloxonium hexachloroantimonates,[58] and alkyl halides in the presence of $SbCl_5$,[55,57] $AgClO_4$,[54,55] dimethyl sulphate,[58–60] and benzoyl chloride[61] (strictly speaking the product in the last case is not an alkoxy-salt but an acyloxydiazenium salt). The alkylation proceeds very readily and smoothly: it is sufficient to mix the reactants in a suitable solvent (CH_2Cl_2, $C_2H_4Cl_2$, etc.) with (sometimes) slight heating. Since the yields of alkoxydiazenium salts are nearly quantitative, no attempts were therefore evidently made to obtain them by other means.

In a dry form alkoxydiazenium salts are crystalline substances; only some of the lowest homologues are oily liquids at room temperature. In the absence of moisture, they can be stored for months without decomposition; they dissolve without decomposition in many solvents, including water, but decompose when the solutions are made alkaline [55]. Their toxicity is lower than that of the initial nitrosamines and is directly proportional to the electrophilicity of the cation. When administered subcutaneously to rats, many alkoxydiazenium salts induce extensive sarcomas[62].

3. Other Sources of Diazenium Salts

N-Nitrosamines form complexes with Lewis acids to which structure (IX), analogous to that of alkoxydiazenium salts, was attributed on the basis of infrared and ^{1}H NMR spectra[63,64]:

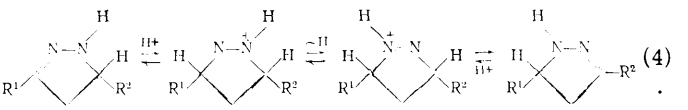


(IX)

A = BF_3, $AgCl_3$, $SbCl_5$, etc.

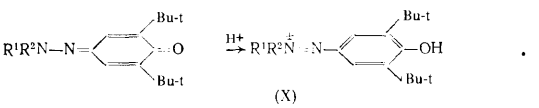
On the basis of the ultraviolet spectra of solutions of dialkylnitrosamines in a trichloroacetic acid-cyclohexane mixture, it has been concluded that nitrosamines are at least partly protonated at the oxygen atom, i.e. that hydroxydiazenium salts are formed[65].

C-Analogues of nitrosamines (hydrazones) are usually protonated and alkylated at nitrogen atoms. Nevertheless, in order to explain the isomeric transformations of 2-pyrazolines in an acid medium, their *C*-protonation with formation of a diazenium fragment has been postulated[66]:



(4)

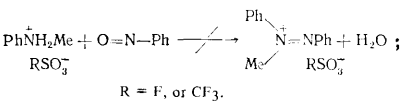
It has also been reported[67] that, when 2,6-di-t-butylbenzoquinone monohydrazones are dissolved in a 1 : 1 CF_3COOH–C_3F_7COOH mixture, trisubstituted diazenium cations (X) are formed:



(X)

However, in this case the closest analogous process is *O*-protonation of *N*-nitrosamines and the cation (X) is a phenylogue of the hydroxydiazenium cation.

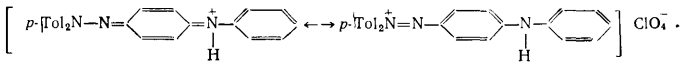
The only attempt hitherto to obtain a diazenium salt by condensing a nitroso-compound with a secondary ammonium salt was unsuccessful[49]:



R = F, or CF_3.

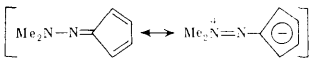
The fragment $\rangle N^+{=}N\langle$ is sometimes present in only one of several limiting structures possible for the given compound. However, if the contribution to the structure is large, the properties of such compounds can be similar to those of the usual diazenium salts. Thus, the dyes of type (XI) isolated by Hünig[5,29,30,68] following the oxidation of 1,1-diarylhydrazines in the presence of aromatic

amines can be assigned to the class of trisubstituted diazenium salts:



(XI)

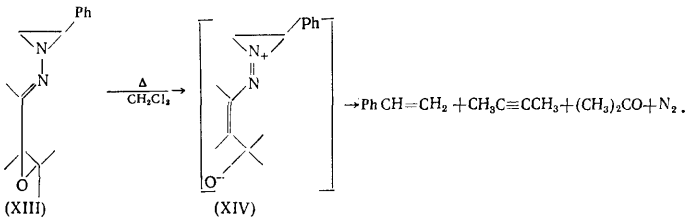
Compounds which can be regarded as a kind of intramolecular diazenium salt are also of interest. An example is the cyclopentadienone dimethylhydrazone (**XII**) [59,60]:



(XIIa) (XIIb)

The appreciable contribution of structure (**XIIb**) is confirmed by the large dipole moment of this compound (3.3 D), which greatly exceeds the dipole moments of the usual hydrazones [69] and can probably be accounted for by the ease of formation of the aromatic cyclopentadienyl anion.

The formation of another intramolecular trisubstituted diazenium salt (**XIV**) is postulated as an intermediate stage in the decomposition of the hydrazone (**XIII**) [70]:



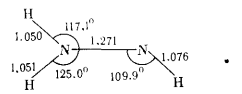
(XIII) (XIV)

Finally, up to 70% of the ions corresponding to the most intense $(M-H)^+$ line in the mass spectrum of the surface ionisation of 1,1-dimethyl-2,2-dideuterohydrazine were formed as a result of the abstraction of a deuterium atom, i.e. had a mass $M-2$, which led to the claim that this ion has the structure of a 1,1-disubstituted diazenium cation [71].

By analogy with the involvement of di- and tri-substituted diazenium cations in a number of reactions of di- and tri-substituted hydrazines, it is suggested that monosubstituted diazenium cations can be formed at intermediate stages of the corresponding reactions of monosubstituted hydrazines. For example, the formation of the methyldiazenium cation has been postulated in the oxidation of methylhydrazine and the decomposition of its tosylate in an acid medium [17]. However, in contrast to di- and tri-substituted diazenium cations, the monosubstituted cations are extremely unstable (if they are formed at all) and there are so far no reliable data concerning their existence.

III. STRUCTURE AND SPECTROSCOPIC CHARACTERISTICS

Almost all the available literature information about the structure of diazenium salts has been obtained by quantum-chemical calculations on their cations. For the simplest diazenium cation $N_2H_3^+$, it has been found by the *ab initio* method on the STO-3G basis as a result of the complete optimisation of the geometry [72] that such species can exist (an energy minimum corresponds to it), is planar, and has the following structure (the bond lengths are quoted in angstroms):



The nitrogen–nitrogen bond length in $N_2H_3^+$ has been determined by the semiempirical CNDO/2 method as 1.23 Å, [73] i.e. somewhat smaller than in the previous case [72]. Apart from the difference between the methods of calculation, the discrepancy may be caused by the fact that Bespalov and Kuznetsov [73] did not carry out a complete optimisation of the geometry and the trigonal hybridisation of both nitrogen atoms adopted in calculations on $N_2H_3^+$ and equal lengths of all the N–H bonds (1.01 Å) constitute a fairly rough simulation of the optimum geometry. The same semiempirical method yielded a structure for the hydroxydiazenium cation with an N=N bond length of 1.24 Å and the preferential transoid conformation with respect to the N–O bond [73]. Despite certain differences, it is seen from the data presented that the N=N bond length in diazenium cations is close to the usual value for the N=N bond in uncharged species (1.238 Å in *trans*-diazene HN=NH). [74]

The electronic structures of a number of simplest substituted diazenium cations have also been calculated by the CNDO/2 method [73]. It has been found that the order of the N=Nπ bond in alkyl- and aryl-substituted cations is very high (0.95–0.96), i.e., in conformity with the canonical structure (I), this is virtually a double bond. In alkoxydiazenium ions the order of the bond is somewhat lower (0.86–0.89) and the multiplicity of the N–O bond is increased, which indicates $p-\pi$ conjugation in these species [73].

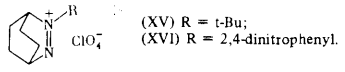
According to the canonical structure (I), the double bond between the nitrogen atoms arises as a result of the "delocalisation" of the lone electron pair of the $N_{(1)}$ atom. However, despite the high order of the π bond, the populations of the p_Z orbitals of the two nitrogen atoms are by no means equal: the population of the p_Z orbital of the $N_{(1)}$ atom remains significantly greater (1.15–1.20 for alkyldiazenium cations and 1.30–1.37 for alkoxydiazenium cations†), while the p_Z orbitals of the $N_{(2)}$ atom are less than unity [73]. The usual formula (I) reflects even less satisfactorily the distribution of the charges on the atoms: it follows from the calculations for a number of cations that the positive charge, formally wholly located at $N_{(1)}$, is to a large extent distributed over the nearest atoms. Such "smearing" of the charge is extremely typical of charged species (see, for example, Haselbach et al. [52]), the charge being distributed mainly in conformity with the electronegativities of the atoms, and ultimately an appreciable proportion of the positive charge is located at hydrogen atoms. For example, according to calculations for azobenzene and the 1,2-diphenyldiazenium cation by the CNDO/2 and MINDO/2 methods, the changes in the charges on two nitrogen atoms on protonation of azobenzene are very similar in magnitude and amount to only 0.13–0.17. [52] These conclusions have been confirmed experimentally: it has been shown by the ESCA method that, when azobenzene is converted into its perchlorate (actually into 1,2-diphenyldiazenium perchlorate), the binding energy of the 1s electrons of the nitrogen atom E_b(N 1 s) increases slightly. E_b(N 1 s) = 404.5 eV for

†Calculations by the Hückel method on 1-aryl-2-methoxy-1-methyldiazenium cations gave a still greater population of the p_Z orbital of $N_{(1)}$—about 1.49. [55]

azobenzene, and the X-ray electronic spectrum of the perchlorate has a broadened band with its centre at 406.7 eV, which is formed as a result of the superposition of two bands separated by approximately 2 eV. The splitting of the band indicates the non-equivalence of the two nitrogen atoms in the perchlorate and the experimental splitting agrees satisfactorily with the value obtained from the calculated charge distribution in the *trans*-1,2-diphenyldiazenium cation[52]. A similar picture is observed in the X-ray electronic spectra of the perchlorates of pyridazine and *o*,*o*′-azobibenzyl (VII).[52]

As a result of the delocalisation of the positive charge in diazenium cations, only a small proportion of it (0.1 to 0.2) remains at the $N_{(1)}$ atom. On the other hand, there is a fairly significant charge on the neighbouring $N_{(2)}$ atom, which is comparable (0.2–0.25) in alkoxydiazenium salts to the charge on the terminal nitrogen atom in the phenyldiazonium cation (0.20) and the carbon atom in immonium ions (approximately 0.2).[73] This apparently determines the ability of alkoxydiazenium salts, like that of diazonium and immonium salts,[75] to undergo coupling reactions (see Section V). At the same time, the comparatively small charge on the $N_{(2)}$ atom in alkyl-substituted diazenium cations (0.03–0.10) suggests a lower reactivity of the corresponding salt in reactions of this type.

The ultraviolet spectrum of 1,1-dimethyldiazenium perchlorate exhibits an absorption at 280 nm ($\epsilon = 150$),[7] while the spectrum of the perchlorate (XV) has λ_{max} 311 nm ($\epsilon \simeq 100$)[50]:



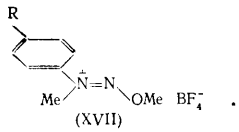
(XV) R = t-Bu;
(XVI) R = 2,4-dinitrophenyl.

The spectrum of 1-methyl-1-phenyldiazenium perchlorate has λ_{max} = 313 nm (ϵ = 6700)[37] and that of 1,1-diphenyldiazenium perchlorate has λ_{max} = 330 nm (ϵ = 9600).[31,37] The bathochromic shift and the hyperchromic effect are exhibited to an even greater extent on passing to salts with three aromatic substituents: the spectra of triphenyldiazenium perchlorate, 1,1-di-*p*-tolyl-2-(*p*-dimethylaminophenyl)diazenium perchlorate, and 1,1-di-*p*-tolyl-2-(*p*-anilinophenyl)diazenium perchlorate (XI) have λ_{max} = 430 nm (ϵ = 15 400),[37,45] 535 nm (ϵ = 55 000), and 556 nm.[29,68] λ_{max} = 232 nm (ϵ = 22 400) has been observed for 1,1-dimethyl-2-(2′,4′-dinitrophenyl)diazenium perchlorate[46] and λ_{max} = 286 nm (ϵ = 7400) has been found for the salt (XVI) in acetonitrile.[50]

The nature of the long-wavelength band in the ultraviolet spectra of alkyldiazenium salts (more precisely their cations) is analogous to that of the long-wavelength absorption of aliphatic azomethines, but not to that of the seemingly similar $n-\pi^*$ transition in saturated azo-compounds[76,77]. In both $\overset{+}{N}{=}N$ and $C{=}N$ groups only one lone electron pair adjoins the π bond and the ultraviolet spectra of compounds of both classes therefore contain bands associated with the $n-\pi^*$-transition having similar energies and extinction coefficients. The appearance in azocompounds of a second lone electron pair at the neighbouring nitrogen atom leads to a qualitatively different picture, since the interaction of the non-bonding orbitals results in the formation of hybrid ψ_+ and ψ_- orbitals. The energy of one of these orbitals is smaller and that of the other approximately just as much greater than the energy of the "pure" *n*-orbital; under these conditions, for example, in *trans*-azomethane, photoelectron spectroscopic data[78] show that the splitting of the non-bonding levels reaches 3 eV. The longest-wavelength transition $\psi_+-\pi^*$ in *trans*-azo-compounds (or the $\psi_--\pi^*$ transition in *cis*-azo-compounds)[78] therefore requires a lower energy than the usual $n-\pi^*$ transition in diazenium cations, while the difference between the symmetries of the ψ_+ or ψ_- orbital, on the one hand, and the virtually localised orbital of the lone electron pair, on the other, leads to a difference in the selection rules and hence in the intensities of the corresponding absorption bands in the ultraviolet spectra of diazenium salts and azo-compounds.

An absorption maximum in the region of 217–226 nm with $\epsilon \simeq (7–9) \times 10^3$ [55] is characteristic of alkoxydiazenium salts with alkyl substituents; it corresponds to the $\psi_2-\psi_3$ transition in the fragment $\overset{+}{N}{=}N{-}O$, whose π-electron system is isoelectronic with that of the allyl anion by virtue of $p-\pi$ conjugation [73]. The ultraviolet spectra of aliphatic alkoxydiazenium salts therefore differ appreciably from those of other diazenium salts, but are similar to the spectra of alkylhydrazones [76,79] and enamines,[80] for which the existence of $p-\pi$ conjugation has been demonstrated[81]. The latter compounds are also isoelectronic with the allyl anion.

If R^1 = Ar in alkoxydiazenium salts, then a bathochromic shift is observed, but the extinction hardly changes. The shift of λ_{max} in the ultraviolet spectra of 1-aryl-2-methoxy-1-methyldiazenium salts (XVII) relative to the absorption band of the compound adopted as the standard is consistent with the results of calculations by the Hückel method[82] and is described satisfactorily by the Hammett equation[55]:



(XVII)

According to ultraviolet spectroscopic data, only diazenium salts with anions exhibiting weak electron-donating properties (I, $X^- = BF_4^-$, ClO_4^-, etc.) are purely ionic. Diazenium cations form ion pairs with more electron-donating anions[7] and a long-wavelength charge-transfer band appears in the ultraviolet spectra of the salts (I, $X^- = Br^-$ or I^-).[50,82] With decrease of the polarity of the solvent, the intensity of this band increases[82]. The absorption maximum shifts towards lower energies as the electron-donating properties of the anion and the electron-accepting properties of the cation are enhanced[50,82].

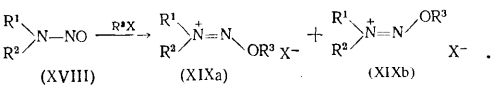
Infrared spectra have been obtained only for alkoxydiazenium salts. Purely aliphatic salts have an intense band at 1540–1575 cm^{-1} in the infrared spectrum[53–55], due to the stretching vibrations of the $\overset{+}{N}{=}N$ bond. For the compound (XVII), this band is weakened and shifts to 1510 cm^{-1}, so that its presence is masked in certain cases by the strong absorption of the aromatic ring at approximately 1500 cm^{-1}. Furthermore, if the anion is BPh_4^- or $SbCl_6^-$, then an intense band, which has been attributed to the stretching vibrations of the N–O bond, is seen in the range 1000–1200 cm^{-1}, usually obscured by the absorption due to the BF_4^- or ClO_4^- anions[55]. On average, the frequency of the stretching vibrations of the $\overset{+}{N}{-}N$ bond in alkoxydiazenium salts proved to be somewhat lower than the stretching vibration frequency of the N=N

bond in aliphatic azo-compounds (1574 cm^{-1} for azomethane[83]), which confirms the conclusion that there is $p-\pi$ conjugation in the $\rangle\overset{+}{N}{=}N{-}O\langle$ system.

The ^1H NMR spectra of diazenium salts have characteristic signals due to protons at the α-carbon atoms of the substituents, but the chemical shifts of the signals to the groups at the neighbouring nitrogen atoms in 1,2-di- and tri-substituted diazenium salts differ very little (0.1 to 0.3 p.p.m.). When $R^3 \neq$ OAlk, the typical range of δ values for α-methyl groups is 4.3–5.1 p.p.m.,[11,15,19,44,49,67] while the signals due to α-methylene (δ = 4.7 to 5.4 p.p.m. for ethyl groups[19,44], and δ = 5.5–6.0 p.p.m. for allyl[44] and benzyl[14] protons) and α-methylidyne protons (δ = 5.6–6.2 p.p.m.[19,44,47]) are located in a weaker field. The same dependence of the chemical shift on the type of α-protons is observed for alkoxydiazenium salts, but the corresponding signals are displaced upfield by approximately 0.5–0.8 p.p.m.[55] On the other hand, the signals of the α-protons of the alkoxy-group in these salts are in the range δ = 4.5–5.2 p.p.m., i.e. in weaker fields than the signals of α-protons in alcohols and ethers (δ = 3.2–4.1 p.p.m.)[84].

The t-butyl substituents at the nitrogen atoms in all the diazenium salts absorb in the region δ = 1.47–1.75 p.p.m.[44,47,51,55] The proton of the N–H group in disubstituted diazenium salts usually gives rise to a common signal with the solvent protons owing to rapid (on the ^1H NMR time scale) exchange. On the other hand, if the exchange can be retarded, then the absorption of the N–H proton is observed in a very weak field (δ = 12.9–16.6 p.p.m.[24,51,52]).

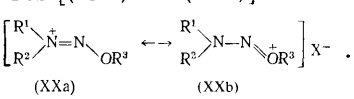
Owing to the high nitrogen–nitrogen bond order, *syn–anti* isomerism is possible for diazenium salts. The ^1H NMR spectra of salts (XIX) therefore contain two signals even for $R^1 = R^2$, corresponding to the protons at the α-carbon atoms of the groups in the *syn*- and *anti*-positions relative to the alkoxy-group[55,58]. The alkylation of nitrosamines (XVIII, $R^1 \neq R^2$), which are themselves usually a mixture of *syn*- and *anti*-isomers, yields, both isomeric alkoxydiazenium salts [(XIXa) and (XIXb)]. An exception is provided by nitrosamines with R^1 = t-Bu where only the *anti*-isomer (XIXa) is formed even for R^3 = Me[55,57]:



(XVIII) (XIXa) (XIXb)

In 1,1-disubstituted diazenium salts, *syn-anti* isomerism has not so far been observed. Under the usual conditions of the recording of the ^1H NMR spectra (HBr/H_2O, 25–30°C), there is a rapid exchange of N–H protons with the solvent and the two substituents R^1 and R^2 give rise to a common signal in the ^1H NMR spectrum. When HBr/H_2O is replaced by DBr/D_2O, the form of the spectrum changes: the lines are broadened and the fine structure of the multiplets is smeared, which can be regarded as a consequence of the slow exchange of protons at the α-carbon atoms of the substituents for deuterium.[19] However, the integral intensity of the signal due to α-protons hardly decreases and in addition it is found that the ^1H NMR spectra in HBr/H_2O assume the same form when the temperature is reduced to 0°C; here too a diffuse signal due to the N–H proton is observed in weak fields ($\delta \simeq$ 16.6 p.p.m.)[24]. Thus the changes in the spectra most probably are not due to the deuterium exchange involving α-protons, but are caused by the retardation of the exchange of the N–H proton with decrease of temperature, or following its replacement by deuterium, which leads to the non-equivalence of the *syn*- and *anti*-substituents. In DBr/D_2O at 0°C the exchange becomes so slow that the signals of the *syn*- and *anti*-substituents in the ^1H NMR spectra of 1,1-diethyl- and 1,1-di-isopropyldiazenium bromides are clearly different. However, for 1,1-dimethyldiazenium bromide, an appreciable signal separation has not been observed even under these conditions[24].

Summarising the calculated and experimental data concerning the diazenium salt structure described above, one may say that, in conformity with the canonical structure (I), the N=N bond in these compounds is virtually a double bond. Owing to the appreciable $p-\pi$ conjugation in the $\overset{+}{N}{=}N{-}O$ fragment, in alkoxydiazenium salts the order of this bond is somewhat lower, so that the structure of such salts should be described, in the language of valence bond schemes, not by one but by a superposition of at least two structures [(XXa) and (XXb)]:



(XXa) (XXb)

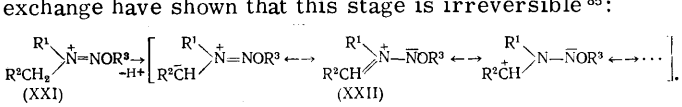
Finally the distribution of charges in diazenium cations is described quite unsatisfactorily by the canonical formula—instead of being located at the $N_{(1)}$ atom, part of the positive charge is "smeared" over neighbouring atoms, which conflicts with the formula.

IV. THE ACID PROPERTIES OF DIAZENIUM CATIONS

The presence of a positive charge in diazenium cations determines in many respects their acid properties. On the one hand, diazenium cations can be regarded as Lewis acids, which accounts for their electrophilic properties and tendency towards the formation of charge-transfer complexes. On the other hand, they can behave as H-acids (Brønsted acids) and the ability to split off a proton also plays an important role in the chemistry of diazenium salts.

The α-protons of the substituents in the $\rangle\overset{+}{N}{=}N\langle$ fragment are extremely acidic. The proton is split off particularly readily from a substituent at the second nitrogen atom. For example, in all reactions which could lead to the trimethyldiazenium cation, only formaldehyde dimethylhydrazone was obtained[17,38]; furthermore, the formation of a 1,2-disubstituted diazenium cation, which readily tautomerises, and the rapid loss of a proton by the latter from the α-carbon atom at $N_{(2)}$ were suggested by Elguero et al.[66] to account for the isomerisation of 2-pyrazolines in an acid medium [reaction (4)]. This is why, among diazenium salts having a proton at the α-carbon atom in the substituent at $N_{(2)}$, only those in which the carbon atom is of a bridge type have been obtained hitherto. The removal of a proton from it is then forbidden by the Bredt rule[47,48,50].

The abstraction of a proton by a nucleophile from an α-carbon atom at $N_{(1)}$ via scheme (5) has been proposed as the first stage in the majority of reactions of alkoxydiazenium salts (XXI),[5] and experiments on deuterium exchange have shown that this stage is irreversible[85]:

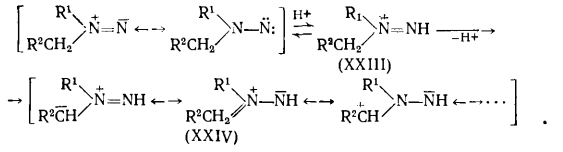


(XXI) (XXII)

(5)

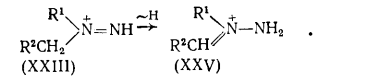
The methyl group in 1,1-dimethyl-2-(2′,4′-dinitrophenyl)-diazenium cations, which have a strong electron-accepting substituent at the second nitrogen atom, is lost very readily [46].

An analogous abstraction of a proton from the α-carbon atom with formation of dipolar azomethineimines (**XXIV**) is believed to be possible for 1,1-disubstituted diazenium cations (**XXIII**) and it is postulated [43,86] as an intermediate stage in the isomerisation of aminonitrenes to azomethine-imines:



(XXIII) (XXIV)

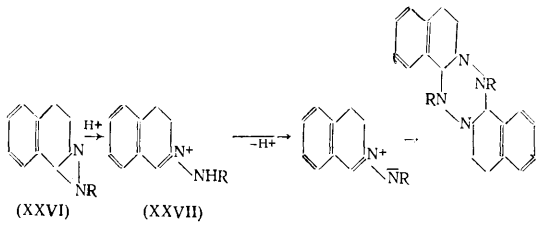
Apart from this, another similar process has also been considered, namely the transfer of an α-proton to the terminal nitrogen atom [15,17-19,24,26,27,46,87]:



(XXIII) (XXV) (6)

The virtually complete absence of the deuterium exchange of α-protons in 1,1-dialkyldiazenium cations in DBr/D_2O [24] is consistent with the results obtained for alkoxydiazenium salts [85] and permits the conclusion that the abstraction of an α-proton from the cation (**XXIII**) is irreversible and the previously postulated [15,18,19,26,27] tautomeric equilibrium (**XXIII**) ⇄ (**XXV**) does not occur in solutions of diazenium salts. The changes in the ^1H NMR spectra of 1,1-dialkyldiazenium salts on passing from HBr/H_2O to DBr/D_2O, which had been treated as a possible consequence of deuterium exchange [19], are induced by the retardation of the exchange of the N–H proton, as stated above‡.

Structures of type (**XXV**), isomeric in relation to the diazenium cations, had already been considered earlier by Schmitz [88-90], who suggested the formation of (**XXVII**) as a result of the opening of the diaziridine ring in (**XXVI**) and also on treatment of *o*-(β-chloroethyl)-benzaldehyde with hydrazine hydrate:

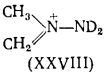


(XXVI) (XXVII)

Under the influence of bases, the cation (**XVII**) splits off a proton to give the corresponding azomethineimine and then dimerisation products, but the salts (**XXVII**) are stable and Schmitz was able to isolate the chloride (**XXVII**, R = Me) [89] and the picrate (**XXVII**, R = H). [90]

‡However, it is claimed [15] that evidence has been obtained for deuterium exchange involving 1,1-dimethyldiazenium bromide in DBr/D_2O and CF_3COOD, although experimental facts are not quoted. It is quite possible that this claim is due to a similar error in the interpretation of the results.

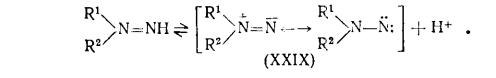
When 1,1-dimethyl-2,2-dideuterohydrazine is ionised by electron impact, more than 95% of the peaks of the $(M-H)^+$ ions are obtained as a result of the abstraction of hydrogen from the methyl group; these ions can be represented as:



(XXVIII)

Their proportion in the surface ionisation spectra is 30%, and the remaining ions of this type arise by the abstraction of deuterium from a nitrogen atom [71].

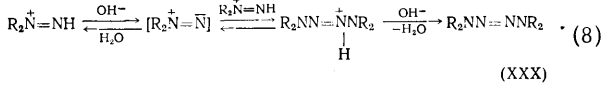
In disubstituted diazenium cations, the loss of the N–H proton is an alternative to the abstraction of protons from the α-carbon atom and the former process is probably reversible and fairly rapid. In the first study on diazenium salts [6] it was already noted that 1,1-disubstituted diazenium cations are N–H acids conjugated with respect to the corresponding aminonitrenes (**XXIX**) and the occurrence of the following acid–base equilibrium in solutions was postulated:



(XXIX) (7)

The position of equilibrium (7) is determined to a first approximation by two factors—the acidity of the medium and the basicity of the aminonitrene (**XXIX**), which depends in its turn on the substituents R^1 and R^2.

The influence of the acidity of the medium can be readily followed. Whereas acid solutions of diazenium salts (I, R^3 = H) are fairly stable in the cold, when they are made alkaline equilibrium (7) shifts to the right with formation of products typical for reactions involving aminonitrenes. Thus, when acid solutions of these salts are neutralised by the addition of a solution of alkali, the corresponding 2-tetrazenes (**XXX**) are formed in high yields [6-10,13,15,20,23,27,28,91], their formation being regarded as a result of the reaction of intermediate aminonitrenes with the surrounding diazenium cations [2,7]:



(XXX) (8)

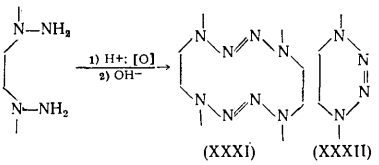
Reaction (8) has been patented as a method for the synthesis of 2-tetrazenes [9], which had been believed hitherto to be its sole products.

However, when the opposite method of neutralisation is used, involving the addition of a solution of the salt (I, R^3 = H) to a solution of alkali, and at a low salt concentration, the yield of the tetrazene is low [7,20], since in this version the aminonitrenes formed virtually lack an environment made up of electrophilic diazenium cations. At the same time, these conditions favour intramolecular transformations of aminonitrenes, as a result of which it is possible to detect virtually the entire set of products typical for reactions involving aminonitrenes: mono- and disubstituted hydrazones, tetrazenes, and geminal azohydrazines [20]. This result constitutes important evidence confirming the formation of aminonitrenes when 1,1-disubstituted diazenium salts are treated with bases and suggests that the neutralisation reactions of acid solutions of these salts can serve as a convenient source of aminonitrenes under extremely mild conditions [20].

The neutralisation of solutions of two different diazenium salts (I, R^3 = H), prepared separately and then mixed, leads to a mixture of all three tetrazenes (symmetrical and asymmetrical) in the statistically expected proportions [6-8,27]. The joint neutralisation of a large number of

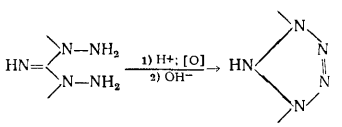
salts leads to a corresponding increase of the number of tetrazenes, and their number is also similar to that expected on statistical grounds [7].

When an attempt was made to synthesise tetrahydrotetrazine (**XXXII**) by the intramolecular closure of the tetrazene chain, only the twelve-membered bistetrazene (**XXXI**) was isolated [91]:



(XXXI) (XXXII)

although, according to McBride's report, the tetrazene fragment was incorporated in the five-membered ring under completely analogous conditions [6]:



The formation of tetrazenes in concentrated solutions of 1,1-dialkyldiazenium salts begins already at pH 0.5–1,[7] so that tetrazenes or the products of other reactions of aminonitrenes, but not diazenium salts, are formed immediately in the oxidation of the corresponding hydrazines in a weakly acid medium.

On passing from 1,1-dialkyl to 1,1-diaryl-diazenium salts, the basicity of the corresponding aminonitrenes should decrease and equilibrium (7) should shift to the right. It may be that, precisely because of this, 1,1-diphenyldiazenium perchlorate is significantly less stable than 1-methyl-1-phenyldiazenium perchlorate [37], since the former should be converted more rapidly into a tetrazene, which readily decomposes further in an acid medium.

The N–H proton of 1,1-disubstituted diazenium cations is also very mobile. Under the influence of nucleophiles, it is readily split off with the regeneration of the initial azo-compound and in the cation it is involved in a rapid exchange between neighbouring nitrogen atoms [51,52].

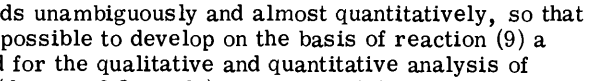
By comparing the tendencies towards the elimination of N–H and α-C–H protons from disubstituted diazenium cations, one may reach the purely qualitative conclusion that in the majority of cases the N–H proton is more acid and mobile. However, virtually no one has made a quantitative comparison of the acidities of these hydrogen atoms and, as shown above, in certain cases one must assume that, even in the presence of the N–H group, a proton may be abstracted preferentially from α-carbon atoms.

V. REACTIONS OF DIAZENIUM SALTS

1. Decomposition Reactions

Information about the decomposition pathways of diazenium salts is fairly contradictory and confused§, probably owing to the large number of secondary reactions in which the primary decomposition products can be involved. It is therefore not surprising that sometimes it is merely concluded that the decomposition of the salts takes place and no attempt is made to establish the structure of the products, let alone the decomposition mechanism [6,13,46].

On the basis of literature data, one can conclude that the first stage in the decomposition of diazenium salts is usually the abstraction of a proton by a nucleophile from the α-carbon atom in the substituent at $N_{(1)}$, already considered, or the transfer of this proton to $N_{(2)}$. The subsequent attack by the nucleophile leads to the dissociation of the highly polarised carbon–nitrogen bond and the decomposition of the diazenium cation. The hydrolysis of 1,1-disubstituted diazenium cations [reaction (9)] apparently proceeds in this way [17,18,26,27], its last stage being analogous to the ready hydrolysis of immonium cations [75,92]:

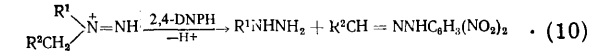


(XXIII) (XXV) (9)

In the cold reaction (9) is virtually negligible but, with increase of temperature, its rate increases rapidly and on boiling hydrolysis terminates in several minutes. 1,1-Diisopropyldiazenium bromide hydrolyses with greater difficulty than salts having primary substituents; if R^1 in (**XXIII**) is a primary group and $R^1 \neq R^2CH_2$, then hydrolysis takes place via both possible pathways, but if R^1 is a secondary group, then R^2CHO and R^1NHNH_2 are formed exclusively [18,26]. In dilute solutions the decomposition proceeds unambiguously and almost quantitatively, so that it was possible to develop on the basis of reaction (9) a method for the qualitative and quantitative analysis of small (down to 0.2 μmole) amounts of 1,1-dialkylhydrazines by determining the carbonyl compounds formed [26].

The hydrolysis products—monoalkylhydrazines and (usually) an aldehyde—can react subsequently with one another, which may be the cause of the appearance of the corresponding monoalkylhydrazones in certain reactions involving 1,1-dialkyldiazenium cations [27,38]. Incidentally, there are no grounds for ruling out other possible pathways leading to the formation of hydrazones, for example, the conversion of the cation (**XXIII**) into the azomethineimine (**XXIV**) with the rearrangement of the latter into a hydrazone, i.e. the reaction can be regarded tentatively as the concluding stage of the so-called "diazene–hydrazone" rearrangement of aminonitrenes [2,86], or the true diazene–hydrazone rearrangement of aminonitrenes, which are involved in equilibrium (7) with 1,1-disubstituted diazenium cations. Then the formation of a monoalkylhydrazone must be regarded as the primary reaction and the monoalkylhydrazine and the aldehyde must be regarded as secondary products of the hydrolysis of the monoalkylhydrazone. If in addition account is taken of the fact that the protonation of the aminonitrene to give a diazenium cation is postulated as one of the intermediate stages in the diazene–hydrazone rearrangement [2] and that there is as yet no satisfactory mechanism for the rearrangement itself [2,5,93], then evidently it would be premature to reach final conclusions about the mechanism of the hydrolysis of 1,1-dialkyldiazenium cations.

When 2,4-dinitrophenylhydrazine (2,4-DNPH) is added to solutions of 1,1-dialkyldiazenium salts, a precipitate of the 2,4-dinitrophenylhydrazone is formed even in the cold, albeit fairly slowly [18,24]:



(10)

§ For example, according to one set of data [6], the decomposition of 1,1-dialkyldiazenium salts in acid solutions is a first-order reaction with respect to the diazenium salt, while in a later study [15] it is mentioned casually that the decomposition of 1,1-dimethyldiazenium bromide in HBr obeys the equation for a second-order reaction with respect to the diazenium salt.

When $R^1 \neq R^2CH_2$, reaction (10) resembles the hydrolytic reaction (9), but the interaction of 1,1-di-isopropyldiazenium bromide with 2,4-DNPH in the cold does not give a precipitate at all[18,24]. One can also postulate at least two mechanisms for the interaction with 2,4-DNPH: preliminary hydrolysis or the direct reaction of 2,4-DNPH with the species (XXV) isomeric with the diazenium cation; a more definite choice cannot as yet be made[24].

The decomposition reactions of alkoxydiazenium[55] and in certain cases trisubstituted diazenium salts[46] in the presence of water are apparently similar to the hydrolysis of 1,1-dialkyldiazenium salts. The preliminary elimination of an α-proton is indicated, for example, by the fact that, with increase of its acidity, the stability of alkoxydiazenium salts diminishes[55]. A mechanism in many respects analogous to reaction (9) has been proposed by Norman et al.[87] for the formation of benzylhydrazine and benzaldehyde in the oxidation of 1,1-dibenzylhydrazine with lead tetra-acetate, which involves the isomerisation of the diazenium cation to a species of type (XXV) and its acetolysis.

Another decomposition pathway, which is usual for 1,1-disubstituted diazenium salts, is the formation of tetrazenes and their subsequent decomposition. This yields primary and secondary amines, aldehydes, and nitrogen[94]. This process plays a notable role in weakly acid or highly concentrated solutions and also for very acidic diazenium cations[6,7,37]. It has also been observed that, after stirring a solution of 1,1-di-isopropyldiazenium bromide at 0°C for 4 h, neutralisation leads to the formation of 60% of di-isopropylamine and only 23% of 1,1,4,4-tetrapropyl-2-tetrazene.[13] The cause and mechanism of such extensive decomposition are obscure.

The decomposition of diazenium cations can result from attack on them by halide ions. Thus it is claimed[17] that 1,1-dialkyldiazenium cations react with Cl^- or Br^- anions in concentrated HCl or HBr with formation of alkyl halides and ultimately of a di-imide which rapidly decomposes under these conditions, reducing some of the reactants:

$$Me_2\overset{+}{N}{=}NH\ \overset{HX}{\longrightarrow}\ MeX + Me\overset{+}{N}H \rightarrow MeX + HN{=}NH \quad . \qquad (11)$$

The reaction is rapid on boiling but, if a solution of 1,1-dimethyldiazenium bromide in HCl is allowed to stand at room temperature, CH_3Cl, CH_3Br, and N_2 are liberated. However, one should note that the total volume of the evolved gases does not exceed 10% of the amount calculated by Eqn.(11) and that the role of such processes is apparently small.

Whereas attack on alkoxydiazenium salts by strong nucleophiles usually begins with the abstraction of a proton from the α-carbon atom of the substituent at $N_{(1)}$, weak nucleophiles remove the substituent at the oxygen atom. Thus the salts (XIX) are readily dealkylated by sulphides to give the initial nitrosamines[58]:

$$\underset{R^2}{\overset{R^1}{>}}\overset{+}{N}{=}NOR^3\ X^- \xrightarrow{R^4_2S} \underset{R^2}{\overset{R^1}{>}}N{-}NO + R^3\overset{+}{S}R^4_2\ X^-$$

(XIX)

while dealkylation by iodide ions proceeds as follows[55,82]:

$$(XIX) \xrightarrow{I^-} \underset{R^2}{\overset{R^1}{>}}N{-}NO + R^3{-}I - X^- \quad . \qquad (12)$$

Reaction (12) is almost instantaneous at room temperature.

Other diazenium salts are also unstable in the presence of iodide ions, because the latter can reduce diazenium cations[15,50]. Furthermore, diazenium cations can be reduced by the primary products of their decomposition or other reactions (examples will be examined below), which also leads to their disappearance.

2. The Reduction of Diazenium Salts

1,1-Disubstituted diazenium salts can be reduced to the initial hydrazinium salts both chemically (with $SnCl_2$[6,28] or HI[15]) and electrochemically[31-33,37,38] with nearly quantitative yields:

$$\underset{R^2}{\overset{R^1}{>}}\overset{+}{N}{=}NH\ X^- \xrightarrow[+2H^+]{+2e^-} \underset{R^2}{\overset{R^1}{>}}N{-}NH_2{\cdot}HX \quad . \qquad (13)$$

The electrochemical reduction of trisubstituted diazenium salts takes place similarly, yielding trisubstituted hydrazines[37,45,46], but the hydrogenation of alkoxydiazenium salts gives rise to disubstituted hydrazines[53,54]. For example:

$$\overset{+}{N}{=}NOEt\ BF_4^- \xrightarrow[MeOH]{H_2/Pt} N{-}NH_2{\cdot}HBF_4 + EtOH \quad .$$

97%

In an aprotic medium the electrochemical reduction of trisubstituted diazenium salts is a one-electron process[44,45,48,82,85] and stops at the stage involving the formation of hydrazyl radicals (XXXIII):

$$\underset{R^2}{\overset{R^1}{>}}\overset{+}{N}{=}N{-}R^3 \xrightarrow{+e^-} \underset{R^2}{\overset{R^1}{>}}N{-}\dot{N}{-}R^3$$

(XXXIII) .

Furthermore, reversible one-electron reduction can be observed also in highly alkaline aqueous solutions but, with decrease of pH, the protonation of the radical (XXXIII) is accelerated and the resulting radical-action is readily reduced to hydrazine—the overall process requires a two-electron mechanism[44].

According to polarographic data, typical half-wave potentials $E_{1/2}$ for the one-electron reduction of alkyldiazenium salts are in the range between −0.5 and −0.8 V,[44,48] the values for salts with phenyl substituents are in the vicinity of 0 V,[31,37,45] and the introduction of the 2,4-dinitrophenyl group into the diazenium cation shifts the half-wave potential to 0.2 V.[46,50] $E_{1/2}$ for 1-aryl-2-methoxy-1-methyldiazenium salts (XVII) varies from −0.35 to −0.04 V, and it has been shown that the dependence of $E_{1/2}$ on the substituent in the aromatic ring is described satisfactorily by the Hammett equation[82]. In one-electron reduction $E_{1/2}$ can be regarded as a quantity characterising the energy of the lowest unoccupied orbital (LUMO) of the diazenium cation to which an electron is in fact transferred. When electron-accepting substituents as well as substituents capable of conjugation, for example, aryl groups, are introduced into the ion, the above energy level is lowered and reduction is correspondingly facilitated; electron-donating substituents have the opposite effect. It is therefore not surprising that the changes in $E_{1/2}$ for the salts (XVII) are also satisfactorily correlated with the LUMO energy differences calculated by the Hückel method[82].

Reduction is a side reaction in many reactions of diazenium salts, other components of the reaction mixture behaving as reductants. For example, it has been found that 1,1-dimethyldiazenium bromide is reduced to the initial hydrazine by acetaldehyde[11]. The primary products of the reaction of 1,1-diphenyl-[33,34] and 1-methyl-1-phenyldiazenium perchlorates[34] with *trans*-stilbene are tetra

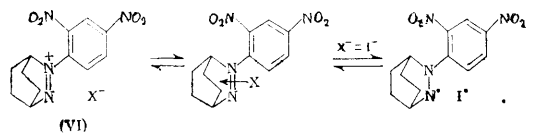
hydrocinnolines; the triazolidines obtained in the reaction with alkoxydiazenium salts with Schiff bases[53,96-98] reduce diazenium salts under the reaction conditions, i.e. diazenium salts can behave as oxidants.

Finally, diazenium cations can be reduced by the counterions, possibly via the formation of donor–acceptor complexes, which we shall now consider.

3. Donor–Acceptor Interactions in Solutions of Diazenium Salts

Depending on the structure of the substituents and the nature of the counter-ion, the group $\overset{+}{N}{=}N$ can behave partially or even completely as an electron acceptor. It has already been stated that, according to ultraviolet spectroscopic data, diazenium cations exist only in solutions of diazenium salts in combination with anions which are poor electron donors in polar solvents. On the other hand, in other cases the diazenium cations form ion pairs and donor–acceptor complexes with the counterions[7,50]. The stability of the complexes and the degree of charge transfer increase with enhancement of the electron-donating properties of the anion, for example, in the sequence $Cl^- < Br^- < I^-$, after the introduction of electron-accepting substituents into the cation, i.e. when the difference between energies of the LUMO of the acceptor (diazenium cation) and the highest occupied orbital (HOMO) of the donor (the counterion) is reduced, and after a decrease of the polarity of the solvent. In the limiting case the electron is fully transferred—one-electron reduction of the diazenium cation takes place and a radical pair is formed.

It has been established[50] that the ultraviolet spectrum of the perchlorate (VI, $X^- = ClO_4^-$) changes little in solvents of different polarities; an intense long-wavelength charge-transfer band appears in the spectrum of the bromide on passing from an aqueous solution to one in acetonitrile and methylene chloride, while the iodide, which is still a salt in water, gives rise to green paramagnetic solutions in non-polar solvents—the ion pair is converted into a radical pair:



(VI)

On the other hand the replacement of the 2,4-dinitrophenol group in (VI, $X^- = I^-$) by the t-butyl group weakens the electron-accepting properties of the cation and complete electron transfer does not take place even in solvents of low polarity[50].

Another example is the interaction of a number of alkoxydiazenium salts (XVII) with NaI.[82] At room temperature rapid dealkylation takes place in accordance with reaction (12), but at −46°C in acetonitrile it is possible to detect the formation of donor–acceptor complexes of alkoxydiazenium cations with I^- ions. Since the HOMO energy of the donor (the iodide ion) is constant in the entire series of complexes, the energy of the charge-transfer band in the ultraviolet spectra changes in parallel with the calculated LUMO energy of the corresponding diazenium cations, and their $E_{1/2}$, as expected[82].

Apparently the same rules hold for exchange processes involving the 1,1-di-alkylhydrazides of sulphonic acids, which have been investigated in detail by Lemal[2,43], who observed that the sulphonic acid residue in hydrazides can be exchanged [reaction (14)] in polar solvents in the presence of sulphinate salts. It has been shown by ^1H NMR that, when solutions of the hydrazide and a sulphinate salt are mixed, the initial rate of exchange is independent of the concentration of the metal sulphinate, which led to the conclusion that the rate-determining stage is the dissociation of the hydrazide into a diazenium cation and a sulphinate anion, i.e. that an S_N1 mechanism operates[43]:

$$\begin{aligned} &\begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!N{-}NHSO_2R^3 + R^4SO_2^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} R^3SO_2^- + \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!\overset{+}{N}{=}NH + R^4SO_2^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \\ &\rightleftarrows \begin{matrix} R^1 \\ R^2 \end{matrix}\!\!>\!N{-}NHSO_2R^4 + R^3SO_2^- \end{aligned} \qquad (14)$$

As a result of exchange with bisulphites, sulphonic acid, 1,1-dialkylhydrazides form little-dissociated sulphuric acid hydrazides, but there is no sign of interaction with effective nucleophiles such as the N_3^-, OCN^-, SCN^-, and $S_2O_3^{2-}$ ions[2,43]. The hypothesis was put forward that the selectivity of the diazenium cations and the stability of the hydrazides obtained are due to the ease of the interaction of the lone electron pair of the $N_{(2)}$ atom with the vacant *d* orbital of sulphur, as a result of which the multiplicity of the N–S bond in hydrazides should be increased. The fact that phosphines, where the phosphorus atom also has vacant *d* orbitals with a suitable energy and could therefore form a partial double bond with a nitrogen atom, give rise to adducts with 1,1-disubstituted[2,43] and trisubstituted[46] diazenium cations was explained from the same standpoints. For example:

$$(RCH_2)_2\overset{+}{N}{-}NC_6H_3(NO_2)_2 \xrightarrow{Ph_3P} (RCH_2)_2N{-}\overset{+}{N}\!\!<\!\!\begin{matrix} PPh_3 \\ C_6H_3(NO_2)_2 \end{matrix}$$

R = H or Ph.

However, in the light of what was said at the beginning of this section, it appears more correct to treat all the instances discussed here as the usual donor–acceptor interaction. Evidently diazenium cations form stable complexes with reducing ions which have a high HOMO and readily give up an electron, reducing the diazenium ion to a hydrazyl residue; on the other hand, the nucleophilic properties of the anion do not in fact play an appreciable role in this instance. Adducts with phosphines are also formed as a result of electron transfer from phosphorus to nitrogen and not conversely; according to the results of Lemal himself, the hydrolysis of these adducts yields the corresponding hydrazines and phosphine oxide[2,43]. The decrease of the tendency of sulphonic acid hydrazides towards dissociation on passing from 1,1-dialkylhydrazides to aryl-substituted compounds and its increase when more electronegative groups are introduced into the sulphonic acid residue[43] is also consistent with the general characteristics of donor–acceptor interactions.

Finally, one may note that, according to some data[34,45] the triphenyldiazenium cation forms a stable complex with pyridine—a compound in which there are no low-lying vacant orbitals capable of interacting effectively with the lone electron pair of $N_{(2)}$ in the diazenium cation. We believe that the existence of the complex, which is fully analogous to the adducts of diazenium cations with phosphines, is ensured by the interaction of the LUMO of the triphenyldiazenium cation with the lone electron pair of the nitrogen atom in pyridine. This is also supported by

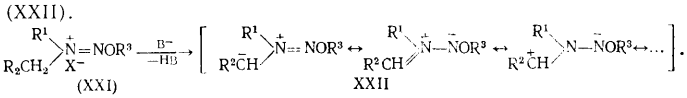
the absence of complex formation with 2,6-lutidine, where the nitrogen atom is sterically shielded[34,45].

It may be that the reduction of 1,1-dimethyldiazenium cations in the KI/HCl system proceeds via a stage involving the formation of donor–acceptor complexes with iodide ions[15] and that in an acid medium two-electron reduction to a hydrazinium salt takes place.

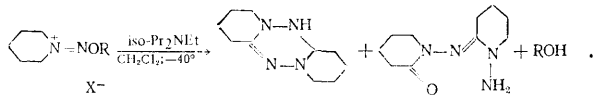
4. Reactions of Diazenium Salts Via 1,3-Dipolar Species

It was already noted above (Section IV) that treatment of diazenium salts with bases can lead to the irreversible abstraction of an α-proton from the substituents at the first nitrogen atom and the formation of 1,3-dipolar species (azomethineimines). Reactions beginning at this stage have been observed for various types of diazenium salts; they are most characteristic of alkoxydiazenium salts (XXI) whose properties are in many respects determined by the subsequent reactions of the corresponding 1,3-dipoles (XXII):

(XXII).

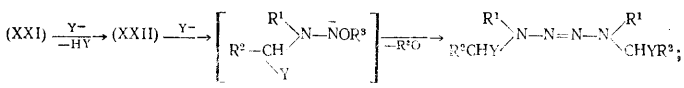


When azomethineimines are generated by weakly nucleophilic bases, dimeric products are obtained, in particular derivatives of 1,2,4,5-tetrazine[5].



For reactions in which the involvement of azomethineimines is postulated, the formation of a fully or partly saturated (most probably as a result of oxidation) tetrazine ring is extremely typical[2,5,99,100]. It was believed previously that perhydrotetrazines are produced by the concerted "head to tail" dimerisation of the azomethineimines themselves, but, firstly, the interaction of two such unstable intermediate species is unlikely for statistical reasons, and, secondly, it has been noted recently[100] that the concerted process is in this instance forbidden. It is therefore most probable that the dimers are the products of the interaction of azomethineimines with the initial compounds.

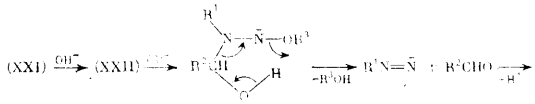
The more nucleophilic bases themselves react with the zwitterions formed initially. Thus treatment of alkoxydiazenium salts in alcoholic solution with alkoxide or azide ions leads to α-substituted tetrazenes[5,101]:

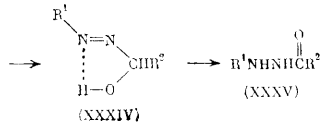


Y = OAlk or N_3.

The mechanism of the last stage is still obscure, but it may be that the reaction proceeds via the corresponding aminonitrene or the 1,1-disubstituted diazenium cation[101].

The products of the interaction of alkoxydiazenium salts and OH^- ions are extremely unexpected[53,57,85,102-104]. Only salts with aliphatic groups undergo this reaction and in the case of acyclic compounds[57,85,103] it leads to *trans*-azoalcohols (XXXIV), for the formation of which the following mechanism has been proposed:





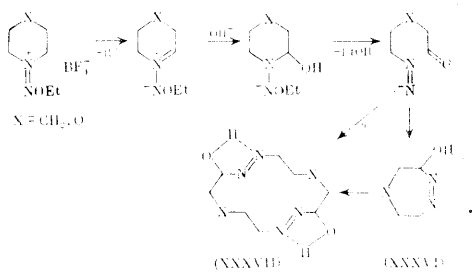
(XXXIV)

(15)

The intermolecular mechanism of reaction (15) has been demonstrated by kinetic data, by the formation of cross-products following the addition to the reaction mixture of both an extraneous monosubstituted diazene and an aldehyde, and also by the independent synthesis of a number of azoalcohols from aldehydes and monosubstituted diazenes[84,103]. It is remarkable that the decomposition into a diazene and an aldehyde strongly resembles the hydrolysis of 1,1-dialkyldiazenium cations examined above, and it can be treated (at least formally) as the hydrolysis of an alkoxydiazenium cation to an aldehyde and an alkoxyhydrazine $R^1NHNHOR^3$ accompanied by the elimination of R^3OH. It is noteworthy that, although 1,1-di-isopropyl-substituted alkoxydiazenium salts are decomposed by aqueous alkali, azoalcohols are not formed in this process[57¶].

Azoalcohols (XXXIV) readily isomerise and only the hydrazide (XXXV) can sometimes be isolated as a result of reaction (15).[84]

All the azoalcohols obtained in this way had the *trans*-configuration, which was additionally stabilised by an intramolecular hydrogen bond. Treatment of the alkoxydiazenium salts obtained from *N*-nitrosopyrrolidines and *N*-nitroso-4,4-dimethylpiperidine with bases should lead (and apparently does so) to cyclic *cis*-azoalcohols, but the latter decompose when an attempt is made to isolate them[103,104]. On the other hand, when derivatives of piperidine itself and morpholine were introduced into reaction (15), the products were not the seven-membered *cis*-azoalcohols (XXXVI), as had been suggested earlier[53], but their dimers—14-membered rings (XXXVII) containing only the N=N *trans*-bonds[102,104]:

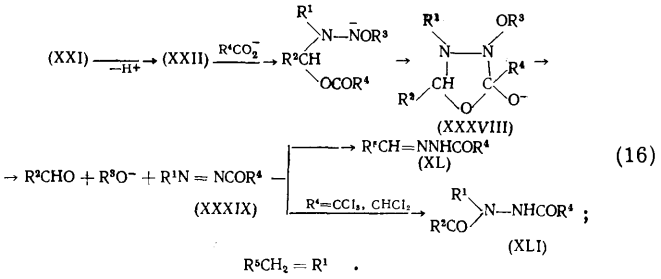


The ultraviolet spectra recorded in the course of the reaction show that the first stage involves the formation of the *cis*-azoalcohol (XXXVI), which is then rapidly converted into compound (XXXVII).[102-104]

The interaction of alkoxydiazenium salts with carboxylate ions gives high yields of acyldiazenes (XXXIX).[106-108] The proposed reaction mechanism involves the formation

¶ The attempts by Hünig to obtain an azoalcohol with a quaternary alcoholic carbon atom from acetone and t-BuN=NH were also unsuccessful[35]. However, it has been recently reported that this reaction has been successfully carried out in the synthesis of MeEtC(OH)N=NPh.[105]

of a five-membered cyclic intermediate complex (XXXVIII) and its decomposition[5,108]:

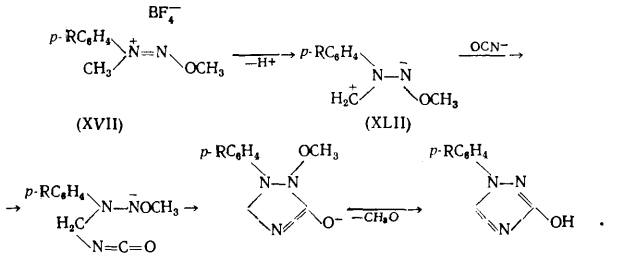


(16)

Reaction (16) depends little on the solvent and on the nature of the substituents R^1, but acyldiazenes can be isolated only when there are no hydrogen atoms at the α-carbon atom in R^1. Otherwise, (XXXIX) immediately isomerises to the acylhydrazone (XL).[107,108] If the primary group R^2CH_2 in (XXI) is replaced by the isopropyl group, the yield of the corresponding acyldiazene falls almost by a factor of two. The anions of both aromatic and aliphatic carboxylic acids readily undergo reaction (16), but for the acetate ion the yield is somewhat lower. According to Hünig the reaction of di- and tri-chloroacetate ions yields initially acyldiazenes, which are apparently capable of recombining with the aldehyde to form the hydrazides (XLI).[108] The interaction of (XXI) with formate ions proceeds quite differently and will be discussed below.

Aryl- and alkyl-acyldiazenes (XXXIX) obtained in this way can serve as a source of monosubstituted diazenes[108,109] and as effective acylating agents. It is therefore significant that reaction (16) takes place to an extent of 80–90% with the anions of *N*-protected aminoacids and can therefore be used to activate them in the synthesis of peptides[108].

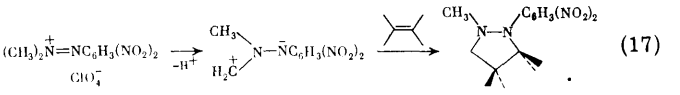
The reaction of 1-aryl-2-methoxy-1-methyldiazenium salts (XVII) with cyanate ions proceeds very similarly to reaction (16).[108] It results in a 40–70% yield of 1-aryl-3-hydroxy-1,2,4-triazoles:



The anomalous behaviour of alkoxydiazenium salts with isopropyl groups in the above reactions is noteworthy. Similar phenomena are observed in the hydrolysis and hydrazinolysis of 1,1-dialkyldiazenium salts—it is also found that salts with secondary groups react much less effectively. The common stage in both cases is usually the initial abstraction of an α-proton, so that one can postulate that the process involving secondary groups is hindered compared with the process involving primary groups. It is still not clear what causes this.

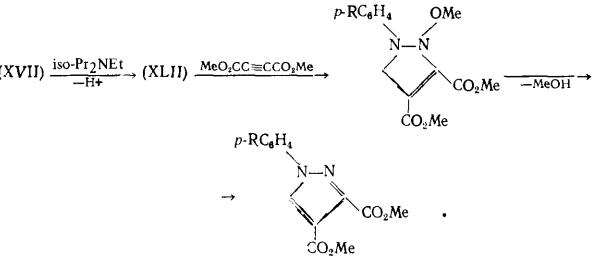
A common property of the azomethineimines obtained from diazenium salts, like that of other 1,3-dipoles, is their ability to undergo 1,3-dipolar addition to multiple bonds, with formation of five-membered heterocycles[99].

The interaction of 1,1-dimethyl-2-(2′,4′-dinitro)phenyldiazenium perchlorate with olefins is of this type[46]:



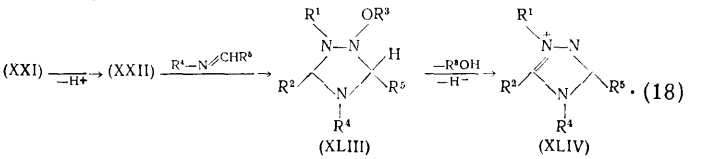
(17)

This is also true of the reactions of alkoxydiazenium salts (XVII) with dimethyl acetylenedicarboxylate[108]:



Reaction (17), involving *cis*- and *trans*-but-2-enes, proceeds with retention of configuration, which supports the operation of a concerted mechanism.

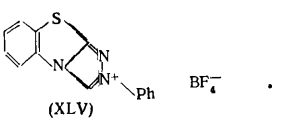
The 1,3-dipolar addition in the interaction of alkoxydiazenium salts with a C=N bond[56,96-98], the final products of which are *s*-triazolium salts (XLIV), has been studied on the greatest scale:



(18)

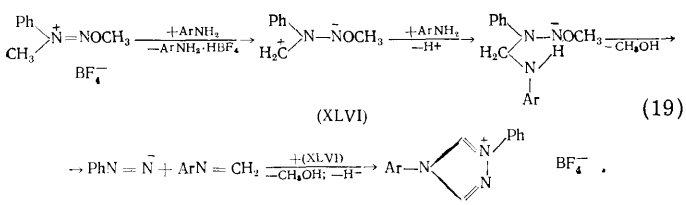
It is believed that a hydride ion is abstracted by the second cation of the diazenium salt in the transition (XLIII) → (XLIV),[56,98] but the yields relative to the initial diazenium salt frequently exceed 50%, so that it is assumed that the cation of the salt (XXI) can combine with more than one hydride ion.

Reaction (18) proceeds best in CH_2Cl_2 at 0–20°C; a proton is abstracted from (XXI) by the imine component itself, for which various nitrogen-containing heterocycles[56,96,97], Schiff bases[96-98], azines and hydrazones[98] have been used. It has been established that any alkoxydiazenium salts (XXI, R^1 = Alk, or Ar, R^2 = Alk) can react with Schiff bases and heterocycles, but only the more reactive 1-aryl-substituted salts (XXI, R^1 = Ar) react with azines and hydrazones[56,98]. Among six-membered heterocycles, pyridine, quinoline, isoquinoline, and phenanthridine have been used; isoquinoline is the most reactive. Five-membered heterocycles (benzoxazole, indole, imidazole, etc.) could not be made to undergo this reaction with one exception: the adduct (XLV) has been obtained in 27% yield from benzothiazole[56]:



Schiff bases can be obtained directly in the reaction mixture from the amine and the aldehyde and the yield does not diminish under these conditions. It has been found possible to obtain *s*-triazolium salt (XLIV) when only the amine was introduced into the reaction. The second component (the aldehyde) is obtained from the

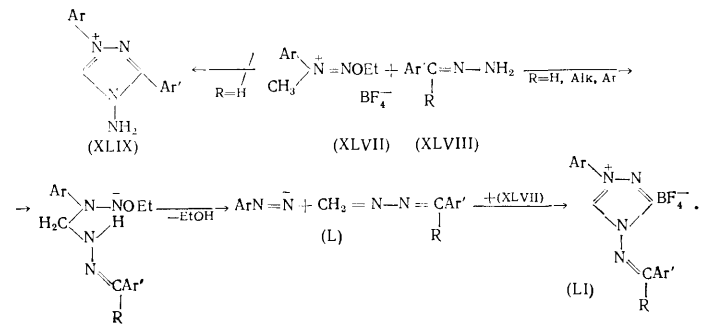
alkoxydiazenium salt by a reaction analogous to reaction (16). For example[56]:



(19)

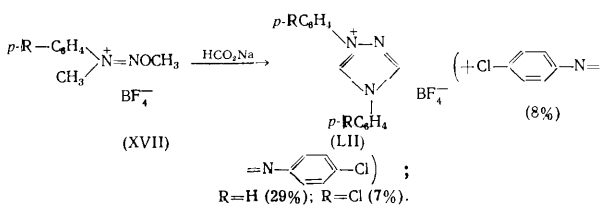
Only one C=N bond of the azines of aromatic aldehydes is involves in reaction (18).[98] The positive charge on the resulting triazolium ring (XLIV) apparently deactivates the remaining imino-group under these conditions. The presence of electron-donating substituents in the azine facilitates the interaction; on the other hand, the azines of nitrobenzaldehydes are inert in relation to alkoxydiazenium salts. Purely aliphatic azines and the azines of aromatic ketones also could not be made to undergo this reaction[98].

It was thought possible to synthesise *N*-aminotriazolium salts (XLIX) from unsubstituted hydrazones (XLVIII). However, contrary to expectation, the mixed azine (L) is formed initially by a process fully analogous to reaction (19) and only then the triazolium salt (LI) can be obtained only from the azine[98]:



The hydrazones of aliphatic carbonyl compounds do not undergo this reaction. Nor was it possible to isolate the products of the interaction of alkoxydiazenium salts with oximes and amidines[98], CS_2, and Ph–N=C=S.[108] It may be that the absence of cycloaddition products in the reactions of certain types of compounds can be accounted for by their low basicity and inability to abstract a proton from the salt (XXI) and to generate the dipole (XXII), rather than their inertness to dipolarophiles. One cannot therefore rule out the possibility that, when a non-nucleophilic base (for example iso-Pr_2NEt) is introduced into the reaction mixture, it is still possible to isolate the corresponding adducts.

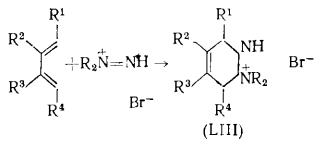
Finally, yet another example of a reaction apparently proceeding via a 1,3-dipolar cycloaddition stage is the interaction of alkoxydiazenium salts (XVII) with formate ions in which it was possible to isolate only small amounts of triazolium salts (LII) containing two aryl residues, instead of the expected formyldiazenes (XXXIX, R^4=H)[56]:



If R = Cl in the salt (XVII), 4,4′-dichloroazobenzene is obtained in addition. The mechanism of this reaction is obscure; it has only been established that, when sodium formate labelled with ^{14}C is used, the triazolium ring does not contain the label[56].

5. Diazenium Cations as Dienophiles

1,1-Dialkyldiazenium cations proved to be very active dienophiles, capable of undergoing the Diels–Alder reaction with many dienes in the cold. This gave satisfactory yields of Δ_4-tetrahydropyridazinium salts (LIII):



(20)

Reaction (20) was discovered by Urry and coworkers[10,11], and was then investigated in detail by other workers[12–14,110] for various dienes and diazenium salts. The yield of (LIII) exceeds 70% in almost all cases and even cyclohexa-1,3-diene, whose reactivity is reduced owing to the incomplete coplanarity of the double bonds in the six-membered ring and which therefore reacts only with very active azodienophiles, gives an adduct with 1,1-dimethyldiazenium bromide in 80% yield. However, reaction (20) does not take place at all with the still less reactive *trans*, *trans*-1,4-diphenylbuta-1,3-diene.[13] The structural specificity of the reaction is usual for diene synthesis: the *ortho*-isomers of the adducts (LIII) are obtained from 1-substituted dienes (piperylene), while the *para*-isomers are obtained from the 2-substituted dienes (isoprene, chloroprene).[10,12–14]

The branching of the alkyl groups in the diazenium cation is apparently important, because 1,1-di-isopropyldiazenium bromide could not be introduced into the synthesis, evidently owing to steric hindrance[13]. The 1,1-dibenzyldiazenium cation reacts in the usual way, but the reaction pathway for aryldiazenium cations changes: instead of diene synthesis, addition to one of the double bonds of the diene, which will be discussed below, takes place instead of diene synthesis[14]. The change in the nature of the interaction is evidently due to the conjugation of the N=N bond with the aryl substituents[14], but it is at present not clear which specific consequences of conjugation are of decisive importance under these conditions.

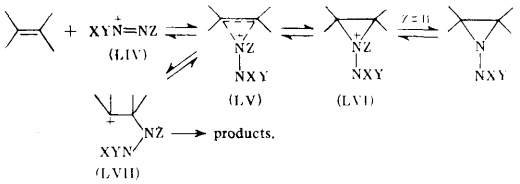
It is known that the diene usually behaves as the donor in the Fiels–Alder reaction, while the dienophile behaves as the electron acceptor. The high reactivity of diazenium cations as well as their analogues—immonium [111] and even diazonium [112] cations—in the Diels–Alder reaction is therefore not surprising.

On another occasion a small amount (12%) of tiglaldehyde dimethylhydrazone was isolated when 1,1-dimethyldiazenium bromide was allowed to react with isoprene [10], but since then nobody has observed the formation of such hydrazones simultaneously with reaction (20).

6. Reactions with Olefins

Formally, the interaction of diazenium salts with olefins can be regarded as the usual reaction of an electrophile (diazenium cation) with a multiple bond. It is therefore not surprising that mechanism (21), proposed to

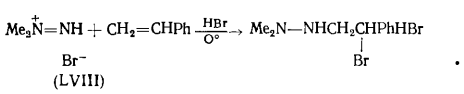
account for such interaction [33,34], is merely a special case of the general mechanism of the addition of electrophiles to unsaturated systems [113] (see also Dolbier [114]):



(21)

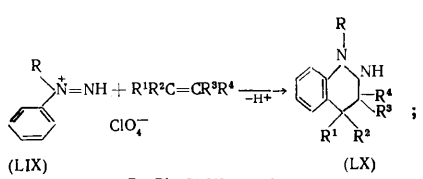
According to mechanism (21), the reaction begins with the attack by the diazenium cation (LIV) on the olefin and the formation of the π-complex (LV), which is in equilibrium with the azidirinium cation (LVI) (in actual fact a σ-complex) and with the carbonium ion (LVII). The positions of all these equilibria and hence the products of reaction (21) are in many respects determined by the structures of the diazenium salts and the olefin [33,34].

In conjugated olefins the substituents are capable of effectively stabilising the positive charge and the equilibrium position shifts in the direction of the ion (LVII). Urry et al. showed [11] that 1,1-dimethyldiazenium bromide (LVIII) reacts with styrene, indene, and 2-phenylpropene to form products, which can be regarded, on the basis of Eqn. (21), as a result of the addition of a bromide ion or water to an intermediate cation of type (LVII). For example:



It has been shown that this reaction is reversible and that the degree of conversion of the olefin and the equilibrium position depend strongly on the solubility of the product and the structure of the olefin. Thus 1-phenylpropene and *trans*-stilbene do not react with compound (LVIII) at all [11].

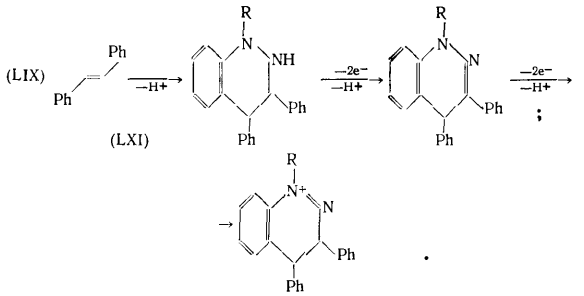
1,1-Diphenyl-, 1-methyl-1-phenyl-, and 1-benzyl-1-phenyl-diazenium perchlorates react quite differently with these olefins in acetonitrile [14,32-36], forming tetrahydrocinnolines (LX):



(22)

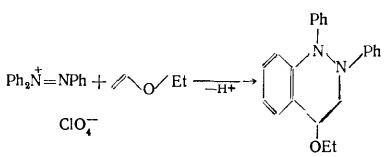
The yields are nearly quantitative when R = Ph and are somewhat lower than R = $PhCH_2$ or Me. Furthermore, the reaction is much slower in the latter case, probably owing to the weaker electrophilic properties of such diazenium cations.

Styrene, indene, 1,1-diphenylethylene, acenaphthalyne, 2-phenylnorbor-2-ene, and tetracyclone (tetraphenylcyclopentadienone) have been introduced into reaction (22). *cis*-Stilbene is inert under these conditions, which is believed [33,34] to be due to steric hindrance, and, although *trans*-stilbene does react, the resulting tetrahydrocinnolines (LXI) are oxidised by diazenium cations to cinnolinium salts:

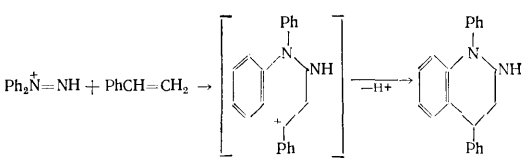


Tetrahydrocinnoline (LXI) was isolated only for R = Me (33%). [34]

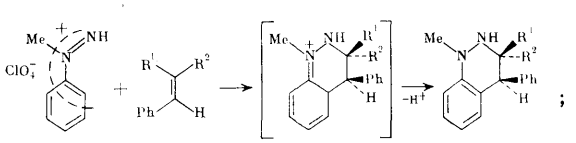
Triphenyldiazenium perchlorate is less reactive than compound (LIX) and does not react with the above olefins; however, its reaction with the more reactive vinyl ether gives the corresponding tetrahydrocinnoline in 95% yield [34,45]:



The formation of tetrahydrocinnolines has been considered, on the basis of mechanism (20), as a result of intramolecular coupling in the intermediate carbonium ion (LVII). [33,34] For example:

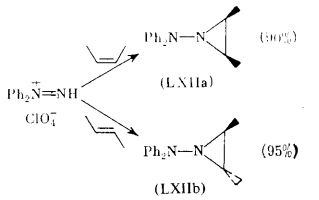


However, according to Zelenin [35], reaction (22) takes place differently and is a concerted [4 + 2] cycloaddition process with the reactants having inverse electronic properties (the so-called "reversed" diene synthesis [115]). Strong evidence in support of this treatment is provided by the complete retention of the configuration of the initial olefin in the tetrahydrocinnoline, which has been demonstrated by the reaction of 1-methyl-1-phenyldiazenium perchlorate with *cis*- and *trans*-β-deuterostyrenes [35]:



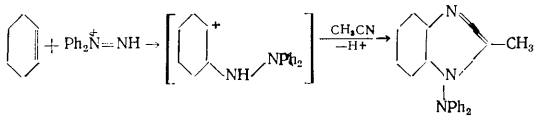
(a) $R^1 = D$, $R^2 = H$; (b) $R^1 = H$, $R^2 = D$.

Only the most electrophilic diazenium cations react with non-conjugated olefins. Thus the reaction of compounds (LIX, R = Ph) with *cis*- and *trans*-but-2-enes in acetonitrile led to the isolation of the aziridines (LXII):



(23)

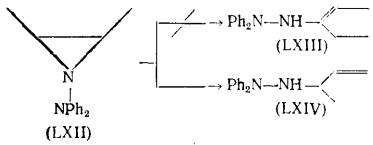
but the reaction with cyclohexane unexpectedly gives an 80% yield of 2-methyl-1-diphenylaminohexahydrobenzimidazole [33,34]:



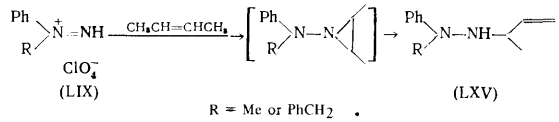
(24)

The difference between the products of reactions (23) and (24) is attributed to steric strain, which reduces in the latter case the stability of the bicyclic aziridinium ion (LVI) [reaction (21)], and to the steric hindrance of the formation of aziridine from cyclohexene. [33,34]

In an acid medium both *cis*- and *trans*-aziridines (LXII) decompose in an extremely non-trivial manner, giving, instead of compound (LXIII), the isomeric hydrazine (LXIV); *trans*-aziridine is much less stable than its *cis*-isomer [33,34]:



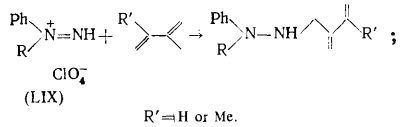
1-Methyl-1-phenyldiazenium perchlorate (LIX, R = Me) does not react with cyclohexene at all and its reaction with *cis*- and *trans*-but-2-enes is much slower than that of (LIX, R = Ph). The corresponding aziridines (LXII) are apparently unstable under these conditions and only the product of their decomposition—a hydrazine (LXV)—can be isolated in approximately 35% yield [34]. 1-Benzyl-1-phenyldiazenium perchlorate reacts similarly with but-2-enes, but the yield of the hydrazine is somewhat higher [14]:



; (25)

R = Me or $PhCH_2$.

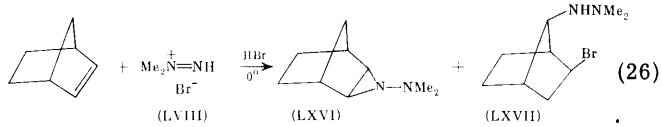
The interaction of aryldiazenium salts (LIX) with 1,3-dienes is apparently analogous to reaction (25). This reaction also leads to the formation of unsaturated hydrazines [14]:



;

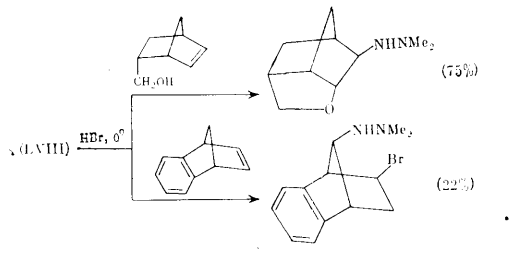
R' = H or Me.

1,1-Dialkyldiazenium salts are evidently less electrophilic than aryldiazenium salts and do not react with the usual olefins. However, the reaction does nevertheless occur with the more reactive double bonds of compounds of the norbornene series. Thus, 1,1-dimethyldiazenium bromide (LVIII) reacts with norbornene to form *exo*-*N*-dimethylaminoaziridine (LXVI) (in 59% yield), and also the bromohydrazine (LXVII) or the corresponding hydrazinoalcohol [15]:

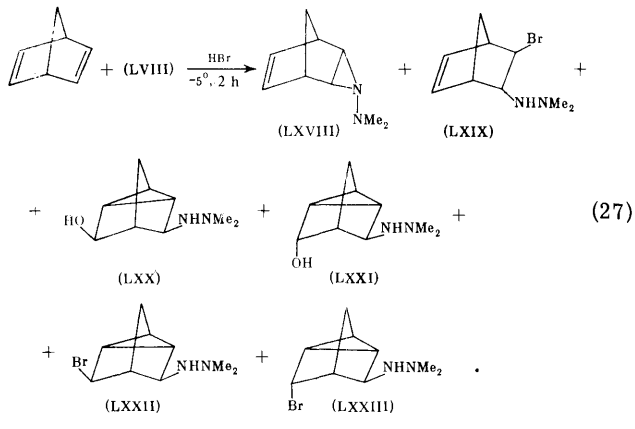


(26)

If account is taken of the possible rearrangements of the norbornyl cations, reaction (26) can be readily accounted for in terms of mechanism (21). The interaction of (LVIII) with *endo*-2-hydroxymethylnorborn-5-ene and benzonorbornadiene also fits satisfactorily within the framework of this mechanism [15]:



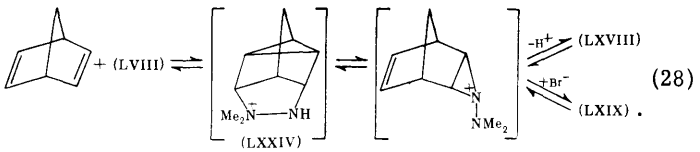
It is noteworthy that in the above examples the first reaction stage is *exo*-attack by the diazenium cation on the norbornene double bond, which is typical for electrophilic addition to such systems. However, the reaction of (LVIII) with norbornadiene yielded the *endo*-aziridine (LXVIII) as well as a series of products of both *endo*-addition [compound (LXIX)] and *exo*-addition [compounds (LXX)–(LXXIII)] with an overall yield in excess of 95% [15]:



(27)

The authors [15] explained the formation of the *endo*-products by the fact that the 1,1-dimethyldiazenium cation can react with norbornadiene not only as an electrophile but also as a dienophile, and that certain reactions of conjugated dienes are characteristic of norbornadiene. It is suggested that the initial [2 + 2 + 2]-cycloaddition product

(**LXXIV**) is subsequently converted into an *endo*-aziridinium ion, which is then transferred into compounds (**LXVIII**) and (**LXIX**):



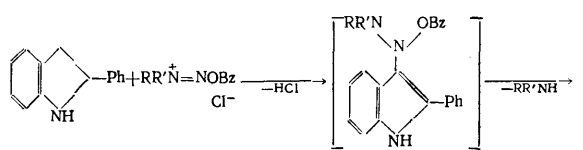
(28)

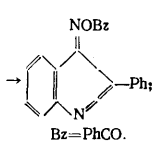
With increase of the HBr concentration, the yield of the *endo*-aziridine (**LXVIII**) falls sharply (from 52% to 0) and, although the amount of (**LXIX**) increases, the *endo* : *exo* ratio in the reaction products diminishes. To explain this, it has been suggested[15] that the dication $Me_2\overset{+}{N}=\overset{+}{N}H_2$ is involved in the reaction; its addition to norbornadiene takes place with formation of an *exo*-adduct, from which all the *exo*-products (**LXX**)–(**LXXIII**) are subsequently obtained.

However, the existence of this dication is extremely unlikely even in a very strongly acid medium and the *exo*-products are most probably formed via a less exotic route. It appears that, when compound (**LVIII**) interacts with norbornadiene cycloaddition [reaction (28)] leading to *endo*-products is accompanied by the usual electrophilic attack at a comparable rate via reaction (26) with formation of an *exo*-π-complex and possibly the corresponding *exo*-aziridine. *exo*-Derivatives of norbornene are known to react with nucleophiles at a rate higher by several orders of magnitude than their *endo*-isomers[116,117], so that *exo*-aziridine should be converted into the decomposition products (**LXX**)–(**LXXIII**) much faster than the *endo*-isomer (**LXVIII**) and its absence from the reaction mixture is quite understandable. It is also possible that the attack by the nucleophile takes place at the stage of the *exo*-π-complex. With increase of HBr concentration, the main role in the alteration of the composition of the products of reaction (27) is apparently played by the increase of the concentration in solution of the extremely nucleophilic bromide ions rather than a change in the pH of the medium.

7. Diazenium Cations in Coupling Reactions

Although coupling reactions are typical for the closest analogues of diazenium salts (diazonium and also immonium salts[75]), there are comparatively few examples of such processes involving diazenium cations. Only the most electrophilic diazenium cations undergo coupling reactions with aromatic compounds. Thus the coupling of benzoyloxydiazenium chlorides (**LXXV**) with 2-phenylindole leads to 3-benzoyloxyimino-2-phenylindolenine[61]:

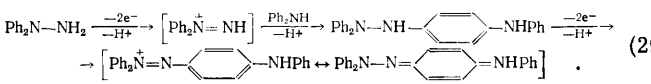




Cyclopentadienone dimethylhydrazone has been obtained from 2-methoxy-1,1-dimethyldiazenium methyl sulphate and cyclopentadienylsodium[59,60]:



Hünig postulated the involvement of 1,1-diaryl-substituted diazenium cations in the oxidative coupling of 1,1-diarylhydrazines wtth aromatic amines, phenols, etc.[5,29,30,68,118]. For example:

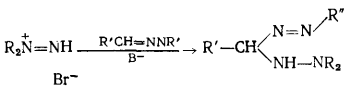


(29)

However, it was already noted above (Section II) that the involvement of diazenium cations in these coupling reactions is fairly controversial, since the oxidation was carried out only in a weakly acid and even in an alkaline medium. The formation of tetrazenes, the typical products of the oxidation of asymmetric hydrazines, competes with the coupling reaction[2-5] and in certain cases only the tetrazene is obtained. The yield of coupling products has amounted to between 10 and 50%.[29,30,68]

When 1,1-dialkyl- and 1-alkyl-1-arylhydrazines, except 1-methyl-1-*p*-nitrophenylhydrazine, are used instead of 1,1-diarylhydrazines, the coupling reaction does not occur at all[29,30]. The attempt to couple 1,1-dimethyldiazenium bromide (**LVIII**) with aniline and phenol in an acid medium was also unsuccessful[11].

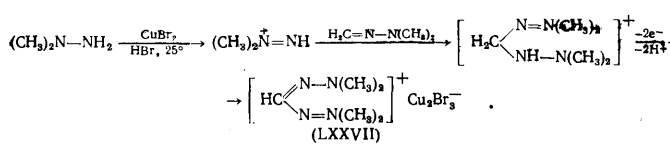
Despite the relatively low reactivity of diazenium salts in relation to aromatic compounds, their interaction with hydrazines takes place smoothly. The coupling of diazonium salts with hydrazones leads to formazans and the corresponding reaction involving diazenium salts was found to lead to the formation of various compounds with the dihydroformazan group. Thus the addition of acid solutions of 1,1-dialkyldiazenium bromides to aldehyde monoalkylhydrazones in the presence of bases led to the synthesis of a series of 3,4-dihydroformazans (**LXXVI**)[20-22,24]:



(30)

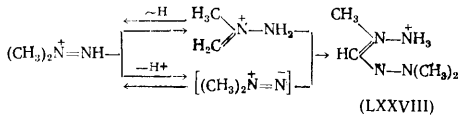
The formation of compound (**LXXVI**) can be treated as a result of the coupling of the hydrazone either directly with the diazenium cation or with the aminonitrene formed from the latter under the influence of the base. It is so far difficult to reach a final conclusion, although the second mechanism is apparently more probable, since compounds (**LXXVI**) have been isolated also following the reaction of hydrazones with aminonitrenes generated in other ways[22].

On the other hand, coupling of the diazenium cation with the hydrazone has been postulated as one of the intermediate stages in the formation of the copper complex of 1,1,5,5-tetramethylformazanium cation (**LXXVII**), which is very similar to reaction (30)[27]:



The structure proposed for (LXXVII) is consistent with the infrared and ^1H NMR spectra as well as X-ray diffraction data. Furthermore, when the complex is decomposed in an alkaline medium, the product is 1,5,5-trimethylformazan—the simplest formazan obtained hitherto[27].

Finally, yet another version of this type of coupling has been put forward by Urry[15]. He believes that the following reactions are possible in a solution of 1,1-dimethyldiazenium bromide [cf. Eqns. (6) and (7)]:



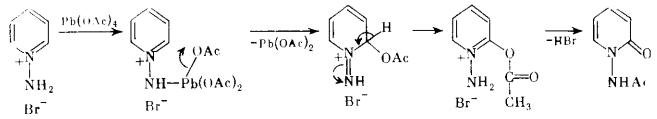
(LXXVIII)

There is no evidence for the structure of the dihydroformazanium ion (LXXVIII) in his paper[15]. It is merely stated that the ion can be hydrolysed to 1,1-dimethylhydrazine, methylhydrazine, and formic acid or can react further to give 1-methyl-1,2,4-triazole and dimethylamine.[15]

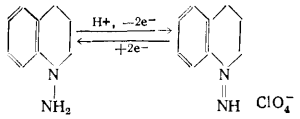
o0o

Several studies on the methods of synthesis and properties of diazenium salts were published in 1977.

The formation of diazenium cations was suggested to account for the oxidation of *N*-aminopyridinium bromide by lead tetra-acetate [119]:



The perchlorate (LXXIX) (λ_{max} = 319 nm, ϵ = 9900),[120] whose properties are in many respects similar to those of 1-alkyl-1-aryldiazenium salts investigated previously, was obtained by the electrochemical oxidation of *N*-amino-1,2,3,4-tetrahydroquinoline in acetonitrile ($E_{1/2}$ = 0.87 V):



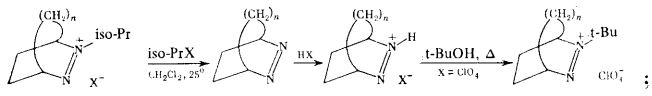
(LXXIX)

Its reduction ($E_{1/2}$ = −0.18 V) regenerates the initial hydrazine in 80% yield and its reaction of type (22) with acenaphthylene, 1,1-diphenylethylene, and indene leads to the corresponding tetrahydrocinnolines (LX) in 54 to 67% yield.

In their study of the mass spectra, generated by electron impact, of various hydrazines, tetrahydrocinnolines (LX), and pyrazolidines, prepared by the condensation of diazenium salts with olefins [reactions (25), (22), and (17) respectively], Cauquis et al.[121] concluded that the main pathway in the fragmentation of the molecular radical-anion is in all cases the retroreaction—the decomposition to the olefin of the diazenium cation or the protonated azomethineimine.

A number of bicyclic trisubstituted diazenium salts (LXXX) were obtained in 90–100% yield by the alkylation of the corresponding azoalkanes with isopropyl bromide in an atmosphere of nitrogen in the presence of $AgClO_4$.

Isopropyl iodide alkylates (LXXXIb) even on simple mixing of the reactants without the addition of a silver salt (yield 86%) [122]:

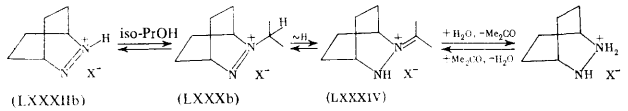


(LXXX, a and b) (LXXXI, a–d) (LXXXII, a–d) (LXXXIII, a–c)

(a) n = 1, (b) 2, (c) 3, (d) 4; X = Cl, Br, I or ClO_4.

When a gaseous hydrogen halide was passed through an ethereal solution of (LXXXI) or the latter was treated with 70% $HClO_4$, the corresponding 1,2-disubstituted diazenium salts (LXXXII) were obtained in 70–100% yield. The trisubstituted salts (LXXXIII) were then synthesised from the perchlorates (LXXXII) in 80–85% yield on refluxing in t-butyl alcohol[122].

The attempt to use the last reaction for the introduction of groups other than t-butyl were unsuccessful: when methyl, ethyl, and isopropyl alcohols were used, (LXXXII) was reduced to hydrazine instead of being alkylated. It has been shown for (LXXXIIb) that the reduction is a reversible process proceeding via stages involving alkylation, isomerisation, to (LXXXIV), and hydrolysis, the rate of equilibration depending on the nature of the anion[122]:



(LXXXIIb) (LXXXb) (LXXXIV)

It is important to note that Snyder et al.[122] were able to isolate a number of salts of the type (LXXXIV) (cf. Section IV).

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*See also Snyder et al.[122]

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The Stereochemistry of Organoarsenic Compounds

F.D.Yambushev and V.I.Savin

The structure of organic compounds of arsenic is considered. Data are presented on the configurational stability and the energy of the inversion barrier in asymmetric arsines. The methods of synthesis of tertiary asymmetric arsenic compounds are surveyed. The results of the separation of asymmetric arsines into optically active isomers and the mechanisms of their transformation as well as the influence of substituents in the benzene ring on the optical activity are described. An analogy is drawn between the stereochemistries of organophosphorus and organoarsenic compounds.
The bibliography includes 220 references.

CONTENTS

I. Introduction 582
II. The structure of arsenic compounds 582
III. Methods of synthesis of chiral organoarsenic compounds 584
IV. Stereochemistry of organoarsenic compounds 587

I. INTRODUCTION

The stereochemistry of organoelemental compounds, which has been developing vigorously recently, is being gradually transformed into an independent section of organic chemistry. This field of stereochemistry is important for the understanding of the general characteristics of optical isomerism and stereochemical transformations, and also in the study of reactivity and reaction mechanisms. Stereochemical problems, particularly those which are associated with the reactions of optically active compounds, have been occupying an increasingly important place in research on the mechanisms of organic reactions. The study of the structure and the chemical and optical properties of asymmetric arsines is one of the urgent problems in this connection.

The number of publications dealing with problems of the stereochemistry of organoarsenic compounds has increased appreciably recently. However, so far there has been no complete compilation of the literature reflecting the state of research in this field during the latest period. The present paper surveys and considers in detail data concerning the structure, methods of synthesis, and the stereochemistry of organoarsenic compounds. Our aim was not an all-embracing discussion of the problem and we endeavoured to concentrate attention on asymmetric arsenic compounds which have been studied systematically recently. In certain cases a comparison is made with the analogous phosphorus compounds.

II. THE STRUCTURE OF ARSENIC COMPOUNDS

As representatives of Group V in the Periodic System, phosphorus and arsenic exhibit certain analogies in the structure of their electron shells. In contrast to its closest analogue—phosphorus in the Third Period, arsenic, which is an element in the Fourth Period, has a completed M shell and an incomplete N electron shell. The following electronic configurations correspond to neutral phosphorus and arsenic atoms:

$$\text{P}—1s^2 2s^2 p^6 3s^2 p^3;\quad \text{As}—1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^3.$$

In neutral phosphorus and arsenic atoms the outer energy levels are not fully occupied by electrons: they contain two electrons with antiparallel spins in the s orbital and only one electron in each of the three p orbitals. The $3d$ orbital in phosphorus atoms and the $4d$ and $4f$ orbitals in arsenic atoms are unoccupied. It is assumed[1] that these orbitals are used in the formation of bonds in the maximum-valence phosphorus and arsenic compounds. Their $4s$, $4p$, and $3d$ orbitals are most available as regards energy for the formation of chemical bonds[2]. Phosphorus and arsenic atoms in their various compounds can be surrounded by between three and six substituents[3].

Within the framework of the present review, organic derivatives of tervalent arsenic as well as individual representatives of quinquevalent arsenic having the structures

$$R_3As,\ R_3As{=}O,\ R_3As{=}S,\text{ and }[R_4As]^{\oplus}X^{\ominus}$$

are considered in greatest detail.

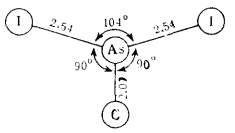
In compounds phosphorus and arsenic atoms have the following electronic configurations: p^3, sp^3, sp^3d, and sp^3d^2. Certain tervalent phosphorus and arsenic compounds, for which the p^3 structure has been postulated, are stable under the usual conditions[4,5]. Examples are provided by phosphine PH_3 and arsine AsH_3. Spectroscopic studies have shown that the hydrogen atoms in the PH_3 and AsH_3 molecules are equivalent and that the H–P–H and H–As–H valence angles are 94° and 92° respectively[6,7]. These angles are greater by 4° in phosphine and 2° in arsine than the angle formed by the overlap of pure p orbitals (90°). Hence it follows that the H–P and H–As bonds are formed with an appreciable involvement of p orbitals and that the lone electron pair is localised predominantly in the s orbitals of phosphorus and arsenic atoms.

Spectroscopic data[7-10] have shown that the replacement of hydrogen by a halogen, alkyl, or aryl in tervalent phosphorus and arsenic compounds leads to an increase of valence angles. The relative content of lone electron pairs of the p type in these compounds increases. The valence angles in trimethyl and trifluoro-derivatives of phosphorus and arsenic increase to 99° and 96° and to 104° and 102° respectively.

The valence angles in certain tervalent phosphorus and arsenic compounds show that there is no significant difference between the types of hybridisation of the lone electron pair orbitals in phosphorus and arsenic. The content of lone electron pairs of the p type in tertiary phosphines and arsines varies near 50%, while in secondary and primary phosphines and arsines it is much less[11]. With

increase of the p character of the lone electron pairs, there is also an increase of the capacity of the hybrid lone pair for p,π conjugation [11].

Comparison of the lengths and energies of arsenic–halogen bonds [10,12–21] shows that shortest and strongest bonds are observed for the F substituent. On passing to Cl, Br, and I, the lengths of the bonds with arsenic increase and there is a corresponding decrease of the dissociation energy. The structure of primary halogenoarsines has been studied in relation to difluoromethyl- and di-iodomethyl-arsines (I). The valence angles and intraatomic distances have been determined by a microwave spectroscopy [22,23].

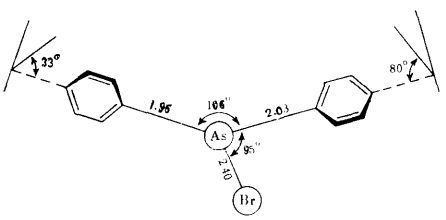


(I)

Among unsaturated compounds, the structure of β-chlorovinyldichloroarsine has been studied by electron diffraction [24]. Appreciable differences in the C–As–Cl valence angles and As–Cl distances relative to saturated compounds were not observed, except that the As–C bond length is reduced (to 1.90 Å). Secondary halogenoarsines were also studied by electron diffraction. In these compounds the C–As–X bond lengths and the valence angle are influenced by the nature of the substituent.

It has been shown [15] that the As–C bond lengths in halogenodimethylarsines $(CH_3)_2As–X$ (where X = Cl, Br, or I) are approximately the same (1.98 Å). The C–As–Cl and C–As–I valence angles are similar, while the C–As–Br valence angle (96°) is smaller than in chloro- and iodo-arsines. The C–As–C valence angle is 96°. [25–27]

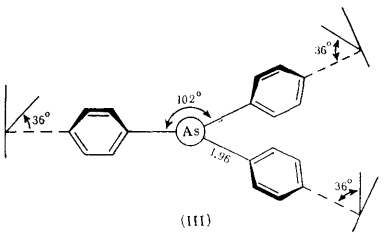
The C–As bonds linking the two aromatic groups in diarylhalogenoarsine molecules are not the same [19,21]. The C–As bond lengths in $(C_6H_5)_2As–Br$ (II) are 1.96 and 2.03 Å. The C–As–C and C–As–Br valence angles are 106° and 95° respectively. The As–Br interatomic distance (2.40 Å) is shorter than in alkylhalogenoarsines. The benzene rings in bromodiphenylarsine are inclined at different angles to the base of the pyramid. Their planes make angles of 33° and 80° with the plane of the base.



(II)

In the series of tertiary aliphatic arsenic derivatives the structure of trimethylarsine $As(CH_3)_3$ has been thoroughly investigated. It has been established by electron diffraction, X-ray diffraction, and microwave spectroscopy [15,27,28] that all the As–C bonds in trimethylarsine are equivalent. The As–C interatomic distances are equal (1.98 Å) and the C–As–C valence angles are the same and amount to 96°.

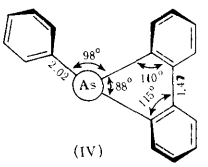
Among aromatic derivatives of tervalent arsenic, the structures of tritolyl arsine (III) and trixylylarsine have been most thoroughly investigated [10,26,29]. The molecules have identical symmetries, similar As–C bond lengths (1.96 and 1.99 Å), and equal (102°) C–As–C valence angles.



(III)

The benzene rings in crystalline tritolyl- and trixylylarsines are located in the plane of the base of the molecule at approximately the same angles, which are 36° and 37° respectively.

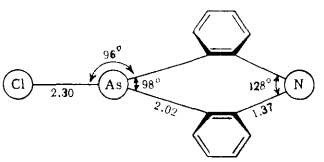
Among cyclic tervalent arsenic compounds, the molecule of 9-phenyl-9-arsafluorene (IV) has been thoroughly investigated.



(IV)

The C–As–C valence angle in the ring is 88°. The length of the C–C bond between the aromatic rings is 1.47 Å. These rings are located in one plane, while the isolated phenyl group is almost perpendicular to it. Its C–As–C valence angle is greater by 10° than the endocyclic angle and the As–C interatomic distances are 2.02 Å.

Among tervalent arsenic compounds with a six-membered ring, the molecule of 10-chloro-5,10-dihydrophenarsazine (V) has been investigated [31].



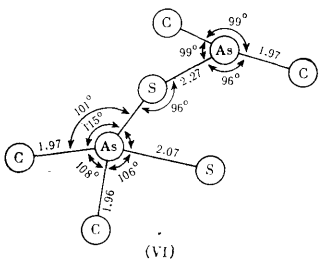
(V)

The three condensed rings do not lie in one plane. The angle of the bend along the As–N axis is 169°. The As–Cl interatomic distance (2.30 Å) is somewhat greater than in $(C_6H_5)_2As–Cl$. The C–N–C angle (128°) is greater than the analogous C–As–C angle (98°). According to Camerman and Trotter [31], the characteristic feature of the molecular structure of this compound can be explained by the interaction of the π electrons of the phenyl groups with the free electron pair of nitrogen and the d orbital of arsenic.

Tetracoordinate arsenic derivatives—sulphides (As=S), oxides (As=O), and arsonium compounds $(=As=)^+X^-$—have a tetrahedral configuration. It has been suggested that $p_\pi–d_\pi$ conjugation is characteristic of the corresponding As=O and As= bonds [32,33].

The two arsenic atoms in the cacodyl disulphide (VI) molecule [34] are in different valence states (As^{III} and As^{V}). Apart from the three substituents surrounding the central

atom, the tetracoordinate arsenic atom has a fourth substituent—sulphur. The C–As=S valence angle is 106° and the As=S bond length (2.07 Å) approaches the As–C bond length (1.96 Å). The C–As–C valence angles are 108°, being similar to the analogous C–As–S angle (106°). The average lengths of all the bonds and all the valence angles in this compound approach the parameters characteristic of a tetrahedral structure.



(VI)

In compounds of quinquevalent phosphorus and arsenic, where the central atom is surrounded by four substituents one of which is linked to it by a double bond, a tendency appears towards the formation of new types of asymmetric molecules. It has been suggested[35] that in compounds of this kind one encounters a new geometrical model, which consists of a distorted tetrahedron with a single double bond directed to one of the vertices. If the three remaining substituents are different, then the molecule has no symmetry plane. Hence it follows that the molecules corresponding to this model are asymmetric and exist in the form of two sterically incompatible optically active isomers. The problem of the optical activity of these compounds is discussed below.

III. METHODS OF SYNTHESIS OF CHIRAL ORGANOARSENIC COMPOUNDS

1. The use of Organometallic Compounds

Of the existing methods of synthesis of tertiary arsines, in the present review we shall consider only those which are used most frequently to synthesise chiral organoarsenic compounds. The commonest method involves the interaction of secondary organoarsenic halides with organic derivatives of Group I, II, and IV metals. In this method sodium can be successfully replaced by other metals: Li, K, Mg, Zn, and Hg.[36-57] Organozinc and organomercury compounds have been recently displaced to an increasing extent by the more readily available and effective for comparative purposes lithium compounds and Grignard reagents[58,59].

When organomagnesium compounds are used, the reaction is usually carried out in ether. Benzene, iso-octane, and tetrahydrofuran are sometimes used successfully. The yield of the required products increases when arsenic iodide compounds are employed[60]. Preliminary dilution of halogenoarsines with dry petroleum ether[61] or benzene[62] also increases the yield of tertiary arsines. Various chiral alkylarylarsines have been synthesised by this method[63-66]:

$$\begin{matrix}\mathrm{Alk}\\ \mathrm{Ar}\end{matrix}\!\!>\!\mathrm{AsCl} + \mathrm{RMgHal} \rightarrow \begin{matrix}\mathrm{Alk}\\ \mathrm{Ar}\end{matrix}\!\!>\!\mathrm{AsR} + \mathrm{MgHalCl} \quad .$$

Under the conditions of the Grignard reaction, chiral arsines can be obtained in high yields by treating a mixture of two Grignard reagents with alkyl- and aryldichloroarsines[67]. Isopropylmethylphenylarsine, for example, was obtained in this way:

$$\mathrm{C_6H_5{-}As}\!\!<\!\!\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} + \mathrm{CH_3MgI} + \text{iso-}\mathrm{C_3H_7MgBr} \xrightarrow{\text{ether/THF}} \text{iso-}\mathrm{C_3H_7{-}As}\!\!<\!\!\begin{matrix}\mathrm{CH_3}\\ \mathrm{C_6H_5}\end{matrix} \quad .$$

The reaction involves the formation of a certain amount of symmetrical arsines. In many instances the method can be more effective than the existing multistage syntheses. The reaction of halogenoarsines with Grignard reagents is used as the principle method for the synthesis of tertiary aliphatic and aromatic arsenic derivatives[68]. Apart from halogenoarsines, the corresponding arsine oxides[69], aminoarsines[70], and arsinic acid esters[71] react similarly with Grignard reagents:

$$\begin{matrix}\mathrm{RO}\\ \mathrm{R'O}\end{matrix}\!\!>\!\mathrm{As{-}OR} + \mathrm{R''MgCl} \rightarrow \begin{matrix}\mathrm{RO}\\ \mathrm{R'O}\end{matrix}\!\!>\!\mathrm{As{-}R''} + \mathrm{ROMgCl} \quad .$$

Grignard reagents are most convenient not only for the synthesis of aliphatic or aromatic arsenic compounds but also for the synthesis of certain other tertiary arsines[72-77], including unsaturated arsines[78-87].

There exist a series of special methods for the synthesis of chiral arsines and their analogues, examples of the use of which are not numerous. They include in the first place the Wurtz–Fittig reaction, which consists in the interaction of halogeno-substituted organoarsenic derivatives with alkyl halides or aryl halides in the presence of metallic sodium. In the field of organoarsenic compounds it is known as the Michaelis condensation[88], Michaelis having used it to synthesise triarylarsines and mixed arsenic compounds without functional groups in the chain. It has been suggested[89] that an intermediate is formed with an As–Na bond, which leads to a tertiary arsine on interaction with an alkyl or aryl halide:

$$\mathrm{RR'As{-}Hal} + 2\mathrm{Na} \leftrightarrow \mathrm{RR'As{-}Na} + \mathrm{NaHal} \quad ,$$
$$\mathrm{RR'As{-}Na} + \mathrm{Hal{-}R''} \rightarrow \mathrm{RR'AsR''} + \mathrm{NaHal} \quad .$$

The yield of the final product is independent of the nature of the halogen, the form of sodium employed playing a more important role[90]; the highest yield is obtained with dispersed sodium[91]. The reaction is carried out in dry benzene, toluene, or ether and is catalysed by ethyl acetate. It is normally used to synthesis triaryl- or alkylaryl-arsines[92-99].

The allyl esters of asymmetric arsinous acid have been synthesised by the reaction of ethylphenylarsine oxide with allyl alcohol[87]:

$$\left(\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{C_6H_5}\end{matrix}\!\!>\!\mathrm{As}\right)_2\mathrm{O} + 2\mathrm{HOCH_2{-}CH{=}CH_2} \rightarrow 2\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{C_6H_5}\end{matrix}\!\!>\!\mathrm{As{-}OCH_2CH{=}CH_2} + \mathrm{H_2O} \quad .$$

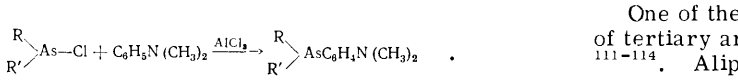
A new method of synthesis of chiral arsines[67] is based on the ability of arsonium salts to alkylate triphenylphosphine:

$$\mathrm{C_6H_5AsCl_2} \xrightarrow[-\mathrm{MgHalCl}]{+2\mathrm{C_6H_5CH_2MgHal}} \mathrm{C_6H_5As(CH_2C_6H_5)_2} \xrightarrow{+\mathrm{RHal}}$$
$$\rightarrow \left[\begin{matrix}\mathrm{C_6H_5CH_2}\\ \mathrm{C_6H_5CH_2}\end{matrix}\!\!>\!\mathrm{As}\!\!<\!\!\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{R}\end{matrix}\right]^{\oplus}\mathrm{Hal}^{\ominus} \xrightarrow[[(\mathrm{C_6H_5})_3\mathrm{PCH_2C_6H_5}]^{\oplus}\mathrm{Hal}^{\ominus}]{(\mathrm{C_6H_5})_3\mathrm{P}} \mathrm{R{-}As}\!\!<\!\!\begin{matrix}\mathrm{C_6H_5}\\ \mathrm{CH_2C_6H_5}\end{matrix};$$
$$\mathrm{R}=\mathrm{CH_3},\ \mathrm{C_2H_5},\ \mathrm{C_3H_7},\ \text{or n-}\mathrm{C_4H_9};\ \mathrm{Hal}=\mathrm{Br}\ \text{or}\ \mathrm{I}.$$

The reaction proceeds under mild conditions in dimethylformamide. The yields of tertiary arsines are nearly quantitative.

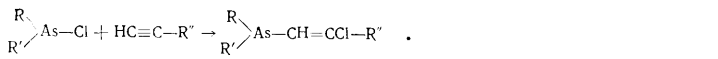
Tertiary arsines have been obtained in fairly high yields by the condensation of secondary chloroarsines with aromatic hydrocarbons in the presence of aluminium

chloride[100,101]. The presence of electron-donating groups in the aromatic ring facilitates the condensation:

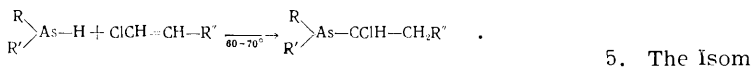


2. Syntheses with Participation of Mobile Atoms

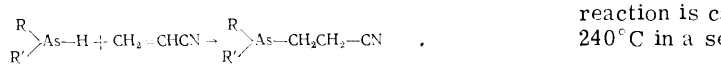
Tertiary arsines with triple carbon–carbon bonds have been synthesised[102] by the direct interaction of acetylene derivatives with halogenoarsines under ultra violet irradiation:



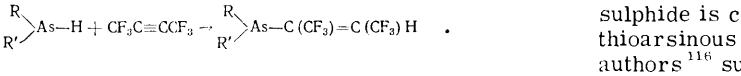
Secondary arsines readily add to chlorine- and fluorine-containing unsaturated hydrocarbons[103–107]. This reaction leads to the formation of tertiary asymmetric arsines in a high yield:



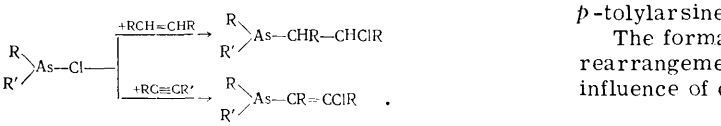
It has been shown[105] that, owing to the mobility of hydrogen, secondary arsines add smoothly to acrylonitrile in the presence of bases with formation of the corresponding chiral arsinonitriles:



The addition of secondary arsines to acetylenic hydrocarbons has been studied in relation to a limited number of examples. It has only been shown that the reaction proceeds readily with formation of tertiary ethylene derivatives of arsenic[102]:

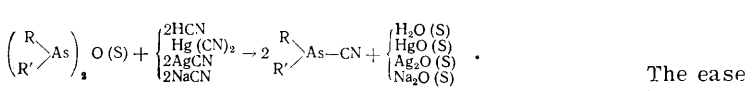


Asymmetric arsines have been obtained[103] by the analogous reaction of secondary halogenoarsines with ethylenic and acetylenic hydrocarbons after prolonged heating at 180°C:



3. Syntheses Based on Hydrocyanic Acid Derivatives

The asymmetric derivatives of tervalent arsenic containing the cyano-group are of interest for the investigation of stereochemical properties. Hydrolysis of arsinonitriles leads to the corresponding carboxy-derivatives of arsenic. The synthesis of tertiary arsines containing a cyano-group linked directly to the arsenic atom is achieved by the interaction of secondary arsine oxides or sulphides with hydrocyanic acid and mercury, silver, and alkali metal cyanides[108–110]:

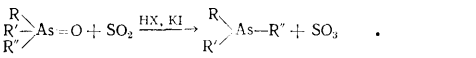


The same compounds can be obtained in high yields also from secondary halogenoarsines[108–110].

4. The Reduction of Arsine Oxides

One of the most convenient methods for the preparation of tertiary arsines involves the reduction of their oxides[111–114]. Aliphatic, aromatic and mixed arsines are obtained by this procedure.

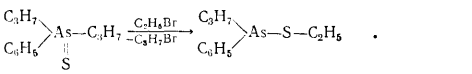
When tervalent arsenic oxides containing three different hydrocarbon groups are reduced, chiral arsines are formed. The reaction is carried out in an acid medium. The reducing agents most frequently employed are sulphur dioxide and tin and the acids are hydrochloric and phosphoric:



The yields of desired products are almost quantitative. When arsine oxides are reduced by sulphur dioxide in hydrochloric acid, an alcoholic solution of iodine or a potassium iodide solution are used as catalysts.

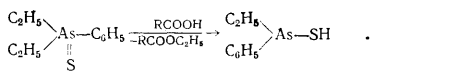
5. The Isomerisation Reaction

Asymmetric compounds containing the =As–S–R linkage are obtained by a rearrangement of alkylarylarsine sulphides on interaction with alkyl halides[115]. The reaction is carried out by heating the reactants at 100 to 240°C in a sealed tube without a solvent for 7–25 h:

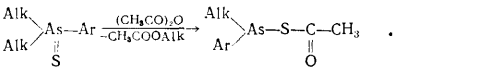


The study of the rearrangement of ethylphenyl-α-naphthylarsine sulphide under the influence of methyl iodide and ethyl bromide established[116] that the arsine sulphide is converted into the ester of the corresponding thioarsinous acid with elimination of the alkyl group. The authors[116] suggest that the reaction pathway can change depending on the reaction conditions. If the reaction is carried out in dry benzene, then the above pathway predominates; however, in the absence of a solvent it proceeds in the opposite direction. Analogous results were obtained[117] in a study of the rearrangement of ethylphenyl-*p*-tolylarsine sulphide.

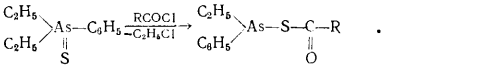
The formation of thioarsinous acids was noted in the rearrangement of diethylphenylarsine sulphide under the influence of carboxylic acids[118]



The rearrangement of dialkylarylarsine sulphides under the influence of carboxylic acid anhydrides[118] leads to the corresponding mixed anhydrides:



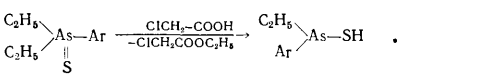
The reaction with carboxylic acid halides takes place similarly[118]:



The ease of reaction depends on the nature of the reactants. Compared with acid anhydrides, the corresponding acid chlorides are more reactive. The reactivity falls with increase in the length of the hydrocarbon chain. For

example, it has not been possible to obtain the products of the isomerisation of diethylphenylarsine sulphide under the influence of palmitoyl chloride.

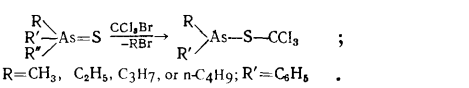
The reaction of diethylphenylarsine sulphide with chloroacetic acids yields the corresponding ethylphenylthioarsinous acids [119,120]:



The rate of reaction increases with increasing number of chlorine atoms in the acid molecule.

It has been shown by differential thermal analysis [121] that the rearrangement [122-124] begins with electrophilic attack by the alkyl group on the sulphur atom. The positive charge, which has arisen on the arsenic atom via an inductive mechanism, polarises the As–C bond, which breaks when attacked by the anion. This results in the formation of the corresponding thioarsinite ester and alkyl halide. The course of the process depends on the nature of the halogen and of the hydrocarbon group.

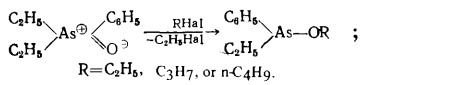
The analogous reactions of dialkylaryl- and trialkylarsine sulphides with bromotrichloromethane have been described [125]. They lead to the formation of the corresponding trichloromethyl esters of asymmetric thioarsinous acids:



It is suggested that, under mild conditions (heating of the reactants in benzene or nitromethane), the reaction proceeds via the mechanism described above, involving the electrophilic attack. The interaction of the above sulphides with bromotrichloromethane at 180°C in a sealed tube can evidently proceed also via a radical mechanism [126-128].

An analogous rearrangement is undergone by arsonic acid esters, for which it was first discovered [129] in 1947, and by arsine oxides [130] although it has been stated in a number of studies [131-133] that the rearrangement of oxides is more complex than that of arsine sulphides. However, in both cases the final reaction products are the corresponding esters.

It has been shown [133] that, when diethylphenylarsine oxide reacts with alkyl bromides, the corresponding esters of ethylphenylarsinous acid are formed in 70% yield:



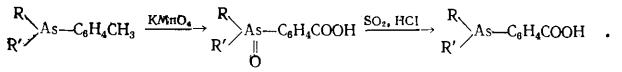
According to the authors [133], the reaction mechanism involves the conversion of diethylphenylarsine oxide into a quasi-arsonium salt, which is then converted further into an ester of ethylphenylarsinous acid with liberation of ethyl halide. The intermediates could not be obtained in a pure form for a long time. The isolation of some of them has been reported only in the latest studies [132,133]. However, the products obtained are extremely unstable under the usual conditions. On exposure to atmospheric moisture, they are converted into oxyarsonium salts with rupture of the O–R bond.

Thus it was shown in the above investigations that the reactions of tertiary arsine sulphides and oxides under the influence of electrophiles take place in the direction opposite to that of the Arbuzov rearrangement [134].

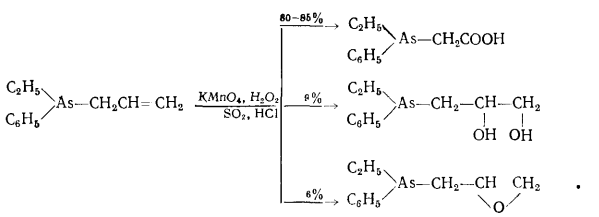
6. Arsines with Functional Groups

Organoarsenic compounds with functional groups, for example arsenic-containing acids or amines, are used in the resolution of racemic arsines with the aid of optically active components.

Asymmetric arsines of the type $RR'AsC_6H_4COOH$ have been synthesised [135-137] by oxidising the corresponding tolylarsines with aqueous $KMnO_4$ and subsequent treatment with gaseous sulphur dioxide in hydrochloric acid:

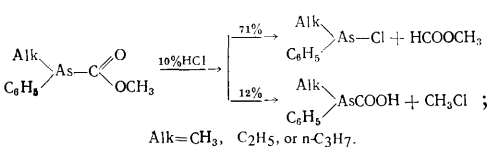


Ethylphenylarsinoacetic acid has been obtained by oxidising allylethylphenylarsine [138] with a solution of $KMnO_4$ and 26% H_2O_2 followed by reduction. This results in the formation of several side products, but ethylphenylarsinoacetic acid is obtained in a high yield:



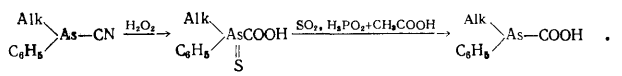
Racemic ethylphenylarsinoacetic acid was isolated from the mixture of products by repeated vacuum distillation.

Alkylarylarsinoformic acids have been obtained [139] by hydrolysing the corresponding esters and nitriles and by carbonating sodium arsenides:

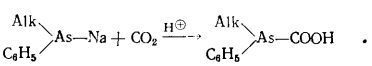


Hydrolysis of methyl ethylphenylarsinoformate with 10% HCl leads to a mixture of products—a halogenoarsine and arsinoformic acid.

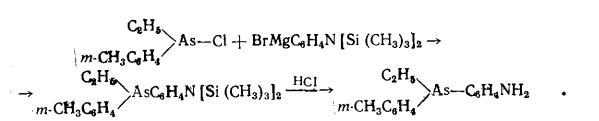
Hydrolysis [110] of arsinonitriles proceeds with formation of arsinoformic acid oxides, which are then reduced by sulphur dioxide to a mixture of hypophosphorus and acetic acids:



When sodium arsenides were carbonated [110], the corresponding arsinoformic acids were obtained in 75% yield:



Asymmetric aminoarsines of the type $RR'AsC_6H_4NH_2$ have been synthesised with the aid of organosodium [140,141] and organomagnesium compounds [142]:



IV. STEREOCHEMISTRY OF ORGANOARSENIC COMPOUNDS

1. Configurational Stability

It was impossible for a long time to obtain stable optically active forms of phosphines and arsines. The difficulty of synthesising optically active phosphorus and arsenic compounds was explained by their low barrier to inversion[143], which apparently occurred via a planar transition state[144].

The inversion frequencies of phosphorus and arsenic hydrides were determined from spectroscopic data[145] (5×10^6 s^{-1} for PH_3, 16×10^4 s^{-1} for AsH_3, 6×10^2 s^{-1} for PD_3, and 30 s^{-1} for AsD_3). Evidently they decrease significantly with increasing mass of the substituents. This shows that the configurational stability should increase on passing to compounds with organic groups. Weston[146] calculated the temperatures at which the racemisation half-life of a number of compounds of Group V elements is 2 h. The temperatures for trimethylphosphine and trimethylarsine are 280° and 380°C respectively and the corresponding energies of the inversion barrier are 22.0 and 29.2 kcal $mole^{-1}$. These values were confirmed also by other workers. It has been shown experimentally[147,148] that, in the racemisation of methyl-n-propylphenylarsine, the inversion barrier reaches 28–30 kcal $mole^{-1}$, which indicates a fairly high configurational stability of tertiary racemisation of methyl-n-propylphenylarsine, the inversion barrier reaches 28–30 kcal $mole^{-1}$, which indicates a fairly high configurational stability of tertiary arsines in non-catalysed thermal racemisation.

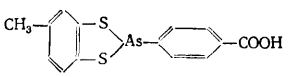
The racemisation of optically active isomers of ethylmethylphenylarsine has been investigated[149] in decalin at 217.6° ± 0.3°C. The activation energy for the inversion of these optical isomers is 42.4 ± 0.5 kcal $mole^{-1}$ at 217.6°C.

It has been shown[150–153] that, on heating at 200°C for 10 h, ethylmethylphenyl- and methylphenyl-n-propylarsines do not lose their optical activity. It has been suggested[150–153] that the calculated racemisation half-life of ethylmethylphenylarsine at 200°C is approximately 740 h. The energy required for the thermal racemisation of the above tertiary arsines should be 59.3–61.0 kcal $mole^{-1}$.

The configurational stability of optically active compounds of Group V elements depends not only on the nature of the central atom but also on the nature of the substituents and the strength of their bonds with the asymmetric atom. For example, it has been shown[154] that, on replacement of one of the three substituents in analogous trisubstitued compounds of nitrogen, phosphorus, and arsenic by groups containing arsenic, phosphorus, silicon, germanium, and tin, the inversion barrier decreases[155].

The configurational stability of arsines and analogous phosphines varies similarly as a function of structure[156] (Table 1). Consequently the electronegativity of the neighbouring heteroatom has a dominant influence on the configurational stability of the above compounds. This is confirmed by the data in Table 1, which show that an increase of the electronegativity of the heteroatom entails an increase of the energy of the barrier. The configurational stability depends also on the $p_\pi - d_\pi$ and $p_\pi - p_\pi$ conjugation of the substituents with the heteroatom[157].

Cyclic compounds of tervalent phosphorus and arsenic exhibit a high configurational stability. The optical activity of these compounds also persists on prolonged heating in non-polar solvents. For example, on heating in chloroform or ethanol, the optical activity of 2-carboxyphenyl-5-methyl-1,3-dithia-2-arsindan (VII) persists, but in an alkaline solution, the compound racemises very rapidly[158].



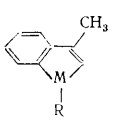
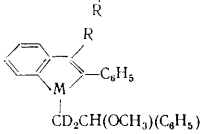
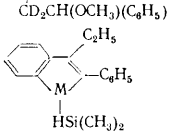
(VII)

According to the authors, the racemisation takes place as a result of the rupture of an As–S bond.

Table 1. Inversion barriers in tertiary arsines and phosphines[156,157].

Compound	Energy of inversion barrier, kcal $mole^{-1}$ (T, °C)	
	E = As	E = P
$(C_6H_5)(CH_3)ER$	43.1 (218)	33.3 (130)
$(C_6H_5)(CH(CH_3)_2)ESi(CH_3)_3$	25.1 (181)	18.9 (62)
$(C_6H_5)(CH(CH_3)_2)EGe(CH_3)_3$	27 (200)	21.4 (109)
$(C_6H_5)(CH(CH_3)_2)ESn(CH_3)_3$	25.9 (191)	19.3 (72)
$(C_6H_5)E(SiH)(CH_3)_2$	17.7 (49)	12.2 (42)

Table 2. Inversion barriers in cyclic arsines and phosphines[159].

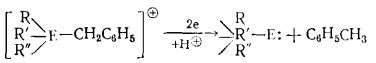
Compound	Energy of inversion barrier, kcal $mole^{-1}$ (T, °C)	
	E = As	E = P
	46.48	35.3 (130)
	35.2 (151)	23.7 (165)
	24.3 (161)	16.6 (180)

The barrier to inversion in certain phospha- and arsaindoles is also lower (Table 2) than for acyclic arsines and phosphines (Table 1).[159] The decrease of the barrier in cyclic compounds probably occurs as a result of the involvement of the free electron pair of phosphorus or arsenic in $(3p_\pi - 2p_\pi)$- or $(4p_\pi - 2p_\pi)$-cyclic delocalisation in the planar transition state.

The configurational stability of optically active phosphines and arsines depends also on the solvent. The probability of the loss of optical properties increases in polar solvents. The process can take place both with complete racemisation and with inversion of configuration.

2. Tertiary Arsines

The positive results obtained in the study of the optical isomerism of cyclic phosphorus and arsenic compounds [160-175] aroused interest in the study of the optical properties or acyclic tertiary phosphines and arsines. Stable enantiomers of the type RR'R'' E were not obtained until 1961.[176-179] They were synthesised by the electrochemical reduction of optically active phosphonium and arsonium salts at a mercury cathode.



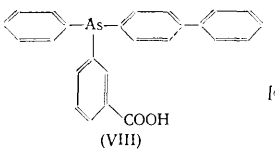
(+) or (−) (+) or (−)

E = P or As

R	R'	R''	$[\alpha]_D^{20}$
CH_3	C_2H_5	C_6H_5	+15.0°
CH_3	C_3H_7	C_6H_5	+16 8°
CH_3	C_2H_5	C_6H_5	+1.9°
CH_3	C_4H_9	C_6H_5	+12.4°

The dextro- and laevo-rotatory isomers of benzyl-n-butylmethylphosphine with the specific rotations $[\alpha]_D^{27} = 24.0°$ and $[\alpha]_D^{27} = -28.2°$ were obtained later [180]. They were synthesised by cleaving with sodium methoxide the optically active (−)- and (+)-isomers of acid benzyl-n-butyl-β-cyanoethylmethylphosphonium dibenzoyltartrates.

The next stage in the development of the stereochemistry of tertiary arsines involved the search for easier methods for the resolution of non-heterocyclic arsines. Asymmetric arsenic derivatives could not be resolved for a long time via their diastereoisomeric salts. The failure was associated with the difficulty of selecting optically active reagents and solvents as well as the appropriate conditions for the fractional crystallisation of diastereoisomeric pairs. An acyclic tervalent arsenic compound (VIII) was resolved only recently using this classical method [181]:



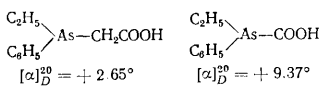
(VIII)

$[\alpha]_D^{20} = +8°$, $[\alpha]_D^{20} = -7°$.

The resolution of triaryl- and alkyldiaryl-arsines containing a functional group (COOH, NH_2) in the aromatic ring has been reported in a number of studies [135-137,182]. (+)-Quinine, (−)-α-phenylethylamine, morphine, and (+)-tartaric acid were used respectively as the asymmetric reagents for the separation of these compounds into optically active isomers. The diastereoisomeric salts were decomposed by treatment with an excess of H_2SO_4 and NH_4OH solutions. The specific rotations of the enantiomers were determined in benzene.

R	R'	R''	$[\alpha]_D^{20}$ (+)	$[\alpha]_D^{20}$ (−)
C_2H_5	$C_{10}H_7$-β	C_6H_4COOH-*o*	6.04°	4.94°
C_2H_5	C_6H_5	C_6H_4COOH-*n*	11.64°	5.35°
C_2H_5	C_3H_7-*n*	C_6H_4COOH-*n*	3.01°	2.12°
C_2H_5	$C_6H_4CH_3$-*o*	$C_6H_4NH_2$-*o*	2.69°	2.34°

Ethylphenylarsinoacetic [138] and arsinoformic [183] acids were resolved similarly with the aid of (−)-α-phenylethylamine and quinine.



$[\alpha]_D^{20} = +2.65°$ $[\alpha]_D^{20} = +9.37°$

3. Tetracoordinate Compounds

The study of the optical properties of phosphonium [184-187] and arsonium [188-190] salts showed that most of them lose their optical rotation in polar solvents (acetone, alcohol), possibly owing to dissociation to the initial phosphines or arsines and the corresponding alkyl halides:

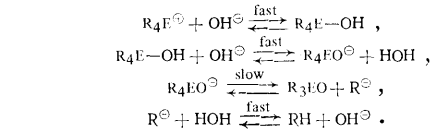


R=CH_3; R'=C_2H_5, R''=C_6H_5; R'''=$C_6H_5CH_2$; Hal=Cl, Br, or I; E = P or As.

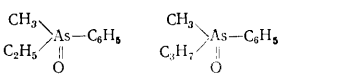
Depending on the nature of the halogen, the rate of racemisation [191] increases in the sequence Cl < Br < I.

The results of the study of the relative configurations of phosphonium and arsonium salts are also of much interest. When optically active tertiary arsines react with alkyl halides, optically active arsonium salts with the same sign of rotation as in the initial arsines are obtained. However, the absolute value of the specific rotation of the salts is greater than that of the initial arsines. This confirms that the hydrocarbon group adds to the arsenic atom via the free electron pair with retention of its relative configuration.

In an alkaline medium optically active phosphonium and arsonium salts are converted into the corresponding oxides [192]. The stereospecific resolution of these salts consists of several stages whose stereochemical mechanism has been examined in detail [193-195]:



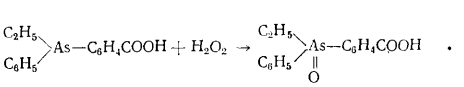
New ways of synthesising optically active tertiary phosphine oxides by the direct oxidation of the corresponding enantiomers have now become available [176]. However, it was for a long time impossible to obtain optically active arsenic oxides with the aid of this method. Horner and Winkler [196] reported the synthesis and a study of the enantiomers of ethylmethyl- and methyl-n-propylphenyl-arsine oxides:



$[\alpha]_D^{20} = +2.4°$ $[\alpha]_D^{20} = +6.4°$; $-18.0°$

It was found that these oxides are optically unstable and racemise rapidly. Evidently the conversion of the oxides into the racemic modification is achieved by their conversion into the hydroxide under the influence of moisture.

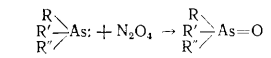
An attempt to obtain optically active tertiary arsine oxides by oxidising the enantiomers of aliphatic-aromatic arsines by H_2O_2 under mild conditions has been reported [197]:



However, the products obtained in this reaction did not exhibit an optical activity.

Owing to the extremely high hygroscopicity of the above oxides, they were synthesised [198] by oxidising optically active tertiary arsines with nitrogen dioxide in dry

nitromethane.

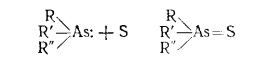


R	R′	R″	$[\alpha]_D^{20}$ (+)	$[\alpha]_D^{20}$ (−)
C_2H_5	C_3H_7-*n*	C_6H_4COOH-*p*	8.63°	7.54°
CH_3	C_6H_5	C_6H_4COOH-*p*	11.84°	9.26°
C_2H_5	C_6H_5	C_6H_4COOH-*p*	13.52°	10.92°
C_2H_5	C_6H_5	C_6H_4COOH-*o*	21.28°	23.59°

The racemisation of the oxides was studied by differential thermal analysis [193,199]. The formation of hydroxides was confirmed on the basis of the differential thermographic curves obtained in the course of the oxidation of (+)-*p*-carboxyphenylethylphenylarsine and the decrease of the specific rotation.

In contrast to their phosphorus analogues, the enantiomers of arsine oxides are optically unstable and show a tendency towards racemisation regardless of the methods and conditions of their synthesis. The rate of racemisation also depends on solvents, increasing in the sequence benzene < chloroform < nitromethane.

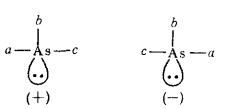
Compared with the oxides, arsenic sulphides are stable. They have been investigated by a number of workers [177,200,201], who were able to resolve them into opically active isomers via diastereoisomeric salts. A convenient method for the synthesis of sulphides, consisting in the interaction of the corresponding arsine with elemental sulphur, has been proposed by Horner and Fuchs [177]. Using this procedure, they obtained from (+)-ethylmethylphenylarsine the enantiomer of its sulphide with the same sign of rotation. Both racemic forms [202] of asymmetric arsenic sulphides [the attempt to separate them chromatographically [203] with the aid of (+)-lactose, (+)-glucose, (+)-starch, and (+)-quartz was unsuccessful] and optically active sulphides [204,205] have been obtained by this procedure.



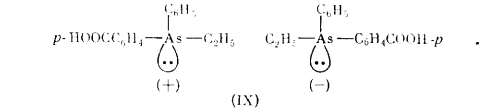
R	R′	R″	$[\alpha]_D^{20}$ (+)	$[\alpha]_D^{20}$ (−)
C_2H_5	C_3H_7-*n*	C_6H_4COOH-*p*	3.84°	4.02°
C_2H_5	C_4H_9-*n*	C_6H_4COOH-*p*	7.32°	7.73°
CH_3	C_6H_5	C_6H_4COOH-*p*	12.50°	9.31°
C_2H_5	C_6H_5	C_6H_4COOH-*p*	19.23°	16.93°

It has been shown that the addition of sulphur to arsenic takes place with retention of the sign of the rotation of the initial enantiomer. It has been established that, when the compounds obtained are heated in benzene at up to 100°C, racemisation does not occur. However, at higher temperatures slow racemisation is observed. It is probably caused by the fact that at high temperatures the enantiomers of the sulphides isomerise to the corresponding thioesters [206].

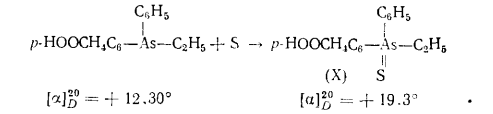
It has been suggested [207] that the (+)-enantiomer has a configuration in which the substituents are arranged in order of their decreasing polarisability in the sequence $a > b > c$. The arrangement of substituents in the opposite sequence corresponds to the (−)-enantiomer.



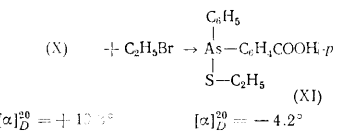
According to this scheme, the molecules of (+)- and (−)-enantiomers of *p*-carboxyphenylethylphenylarsine (IX) have the following form:



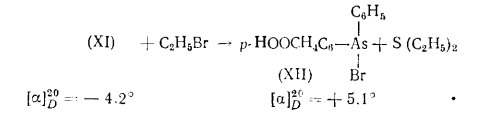
The relative configuration of (IX) has been studied [207] with the aid of the reaction of the (+)-enantiomer with sulphur:



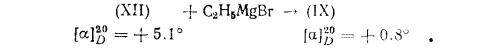
The formation of the (+)-enantiomer of the sulphide (X) with a high specific rotation is due to the increase of the asymmetry of the entire molecule, since the reaction takes place with retention of the relative configuration of the initial product. The interaction of (+)-(X) with ethyl bromide leads to the formation of a product with the opposite sign of rotation [204]. The explanation is that the reaction proceeds via a bimolecular mechanism, involving the bonds between the asymmetric arsenic atom and two substituents. The substituents are arranged during the reaction in a sequence which is different from that obtaining before the reaction. This is accompanied by the inversion of the configuration and a change in the sign of rotation.



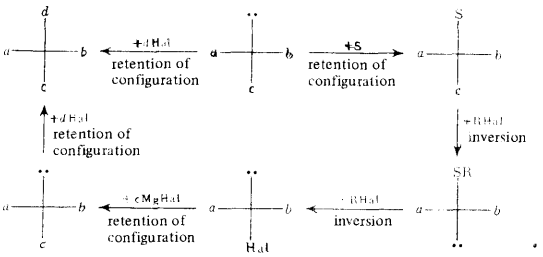
On treatment with ethyl bromide, (−)-(XI) undergoes a further transformation, which leads to the formation of dextrorotatory phenyl-*p*-carboxyphenylbromoarsine (XII) [207]:



(XII) reacts with ethylmagnesium bromide to form compound (IX) with the same sign of rotation:

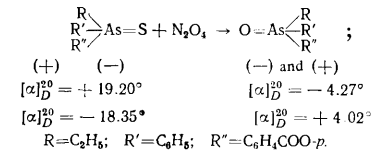


The above cycle of transformations takes place in accordance with the following scheme:

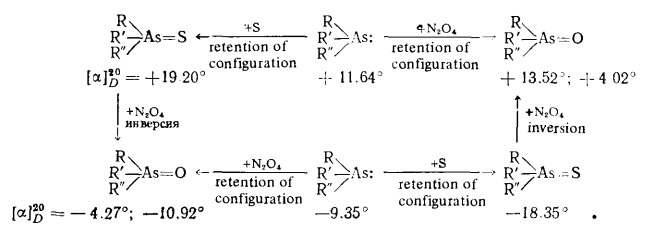


The reaction of optically active sulphides with N_2O_4 [198] in nitromethane at −15°C leads to the formation of the

corresponding oxides with the opposite sign of rotation:

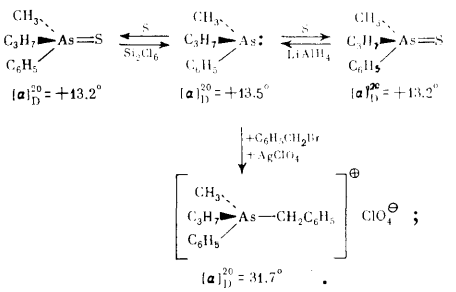


This reaction is accompanied by an inversion of configuration, which follows from the data below:

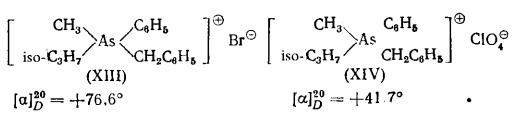


The optically active oxides of acyclic phosphines are reduced stereospecifically by hexachlorodisilane to the corresponding phosphines with inversion of configuration [208]. The reduction of methylphenyl-n-propylarsine sulphide, which has the *R* configuration, with hexachlorodisilane and lithium tetrahydroaluminate proceeds with almost complete retention of configuration at the arsenic atom [209]. The above transformations have been achieved under mild conditions in tetrahydrofuran and di-n-butyl ether.

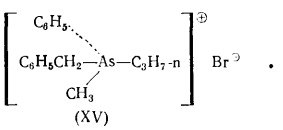
The stereospecific transformations of the arsenic compounds under consideration are illustrated schematically below:



The absolute configuration of chiral isopropylmethylphenylarsonium salts has been determined by the method of quasi-racemates [210]. These salts have been obtained by the reaction of the corresponding diastereoisomers of acid D-(−)- and L-(+)-arsonium dibenzoyltartrates with ammonium bromide and perchlorate in methanol. This led to the isolation of dextro- and laevo-rotatory benzylisopropylmethylphenylarsonium bromide (XIII) and the dextro-rotatory perchlorate (XIV):



The dextro-rotatory benzylmethylphenyl-n-propylarsonium bromide (XV) has the *S*-configuration [211]:



However, when the n-propyl group is replaced by the isopropyl group, the molecular configuration may be inverted [210]. The fusion diagram (Fig. 1) for mixtures of enantiomers of benzylmethylphenyl-n-propylarsonium bromide (XV) with $[\alpha]_D^{20} = +33.4°$ and $[\alpha]_D^{20} = -33.0°$ shows that the enantiomers have a melting point of 188°C, while the racemate melts at 170°C; the eutectic composition is 31% of the (+)-isomer and 69% of the (−)-isomer of compound (XV).

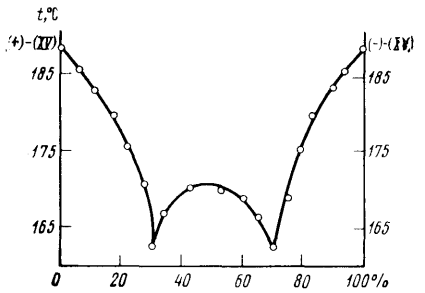


Figure 1. Fusion diagram for a mixture of enantiomers of benzylmethylphenyl-n-propylarsonium bromide (XV).

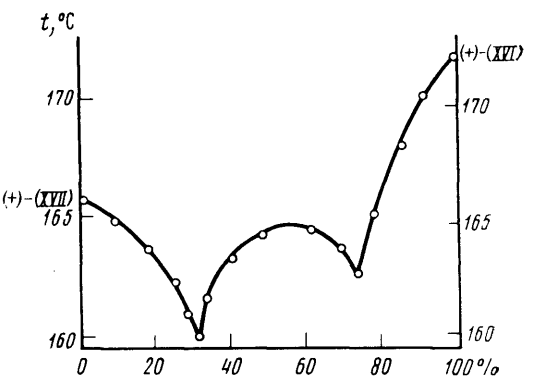


Figure 2. Fusion diagram for a mixture of (+)-(XVI) and (+)-(XVII) tetraphenylborates.

Dextro- and laevo-rotatory benzylmethylphenyl-n-propylarsonium tetraphenylborates (XVI) melt at 172°C, while (+)-benzylisopropylmethylphenylarsonium tetraphenylborate (XVII) has a melting point of 166°C. The fusion diagram (Fig. 2), obtained by combining (XVI) and (XVII) in various proportions, is characteristic of a quasi-racemate with two eutectics melting at 160° and

163°C. This phenomenon shows that the mixture components have the opposite configurations. The same conclusions can be arrived at by comparison with the fusion diagram (Fig. 3) of mixtures of the (+)- and (−)-tetraphenylborates (XVI) in various proportions.

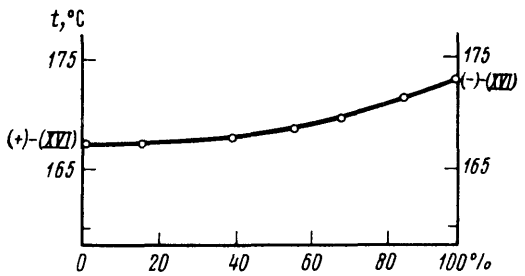
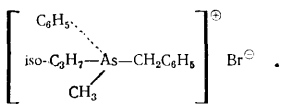


Figure 3. Fusion diagram for a mixture of (+)- and (−)-(XVI) tetraphenylborates.

The above arguments lead to the conclusion that benzylisopropylmethylphenylarsonium (XIII) has the *R*-configuration:



4. The Influence of Substituents in the Benzene Ring on the Optical Activity

It is of definite interest to establish a relation between the structure and the optical rotation of the molecule, which can be followed by introducing various substituents into the aromatic ring joined to the asymmetric atom.

The data in Table 3 show that the absolute specific rotations of *o*-, *m*-, and *p*-carboxy-, methoxycarbonyl-, bromo-, and amino-substituted arylarsines and their sulphides decrease steadily [212-217], although the change is sometimes very slight. When the optical rotations of carboxy-derivatives of arsines and their methyl esters are compared, the specific rotation of the latter is found to be higher than that of the initial arsines. This is probably associated with the increase of the asymmetry of the molecule due to the bulky ester group. The optical rotation of the sulphide is higher than that of the initial arsine enantiomers. This can also be attributed to the increase of the asymmetry of the molecule.

Presumably the change in the optical activities of the above compounds occurs in consequence of the steric influence [218,219] of the substituents on the internal rotation of the groups linked to the asymmetric arsenic atom. The process is evidently accompanied by a change in the "normal" angle of rotation of the aromatic rings. This hypothesis arose when Stuart–Briegleb models were examined. The close proximity of the carboxy-group to the arsenic atom in *ortho*-isomers retards the internal rotation of the groups about the As–C bond axis, which reduces the possibility of the rotation of the phenyl groups and can increase the optical activity of the molecule. In the *meta*-substituted compound the carboxy-group is quite remote from the asymmetric As atom, so that its influence on the attainment of a hindered conformation and the optical activity is diminished. On the other hand, the steric effects due to the presence of two phenyl groups remain, although free rotation remains possible for the ethyl group. In the molecule of the *para*-substituted compound the influence of the carboxy-group on the optical activity is reduced to a minimum, which has been confirmed by the specific rotation.

Table 3. Specific rotations of chiral arsenic compounds of the type $XC_6H_4(C_2H_5)AsC_6H_4Y$. [212-219]
(Z)

X	Y	Z	$[\alpha]_D^{20}$, °	X	Y	Z	$[\alpha]_D^{20}$, °
H	*o*-COOH	LEP*	+18.36; −18.45	H	*o*-COOH	S	+25.21; −24.81
H	*m*-COOH	LEP	+16.63; −16.41	H	*m*-COOH	S	+23.75; −23.08
H	*p*-COOH	LEP	+12.75; −11.86	H	*p*-COOH	S	+22.56; −21.98
H	*o*-$COOCH_3$	LEP	+25.27; −25.34	*o*-Br	*p*-COOH	S	+23.43; −23.12
H	*m*-$COOCH_3$	LEP	+22.61; −22.30	*m*-Br	*p*-COOH	S	+22.50; −21.88
H	*p*-$COOCH_3$	LEP	+17.44; −17.20	*p*-Br	*p*-COOH	S	+20.40; −19.33
o-Br	*p*-COOH	LEP	+16.80; −16.20	*p*-CH_3	*o*-NH_2	S	+2.81; −2.78
m-Br	*p*-COOH	LEP	+15.20; −14.91	*p*-CH_3	*m*-NH_2	S	+2.49; −2.40
p-Br	*p*-COOH	LEP	+13.54; −13.10	*p*-CH_3	*p*-NH_2	S	+2.23; −1.94
o-CH_3	*o*-NH_2	LEP	+2.69; −2.34	—	—	—	—
o-CH_3	*m*-NH_2	LEP	+2.46; −2.03	—	—	—	—
o-CH_3	*p*-NH_2	LEP	+2.24; −1.72	—	—	—	—

*LEP = lone electron pair.

Table 4. Parameters of the molecular motions of certain tervalent arsenic compounds of the type $RR'AsC_6H_4R''$ according to NMR data [220].

R	R'	Mobile group	T (°C) corresponding to T_1^{min}	T_1^{min}, μs	$T_{1\rho}$, s	Activation energy for reorientation, kcal mole^{-1}
Cl	Cl	H	−29	85	—	—
Cl	Cl	CH_3-*m*	−23	58	—	—
Cl	Cl	OCH_3-*o*	−85	54	$4.2\cdot10^{-13}$	3.35
C_2H_5	Cl	CH_3-*p*	−23	52	$5.6\cdot10^{-15}$	4.6
C_2H_5	Cl	OCH_3-*p*	−105	120	—	—
			−27	52	—	—
			−83	84	$4.2\cdot10^{-13}$	3.35
C_2H_5	C_6H_5	CH_3, CH_3, N	−103	79	$5.6\cdot10^{-15}$	4.6
			−46	43	—	—
			−83	78	$5.6\cdot10^{-15}$	4.6
			−134	82	—	—

The possibility of the rotation of the phenyl group about the As–C bond has been studied [220] by NMR. The specimens used were compounds of tervalent arsenic of the type RR'AsCl and RR'R''As (Table 4), where R = C_6H_5, *p*- and *m*-$CH_3C_6H_4$, or *p*- and *o*-$CH_3OC_6H_4$, R' = C_2H_5, and R'' = $N(CH_3)_2$, for which the spin–lattice relaxation times T_1 and $T_{1\rho}$ were measured. The second moments of the NMR line were calculated by analysing the solid-echo signals. The measurements were made on an NMR pulse spectrometer at a frequency of 27.5 MHz in the temperature range from −190°C to +20°C.

Several relaxation regions, associated with individual forms of intramolecular motion, were observed for all the test specimens. All the arsines containing the ethyl group give rise to a minimum at $10^3 T^{-1} = 6$ on the curve relating the relaxation time to temperature, while for specimens without this group there is no such minimum. This makes it possible to assign the given relaxation region to reorientations of the ethyl group about the As–C bond. Substances containing the methoxy-group exhibit a minimum at $10^3 T^{-1} = 5.5$, which is associated with the mobility of the methoxy-group. The compound containing the dimethylamino-group has a relaxation region at $10^3 T^{-1} = 5.5$ associated with its rotation. At higher temperatures all the specimens exhibit a relaxation period T_1 associated with the mobility of the molecule as a whole. At the temperatures investigated the relaxation regions associated with the mobility of the benzene ring were not observed. The absence of a minimum on the curves for the temperature variation of T_1 and $T_{1\rho}$, corresponding to compounds with a phenyl group, may indicate a greater degree of retardation of the rotation of the aromatic rings. Consequently one can postulate that steric factors hinder the reorientation of the aromatic groups and determine their angle of rotation. This can be in turn one of the causes which determine the angle of rotation of optically active compounds.

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Electrophotographic Phenomena in Linear Polymers with Saturated and Conjugated Bonds

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The possibilities of varying the most important characteristics of organic polymers-electronic absorption spectra and the spectra of the quantum yield of the internal photoeffect, which to a large extent determine the limiting light sensitivity of silver-free and in the first place electrophotographic processes, are examined. The ways of increasing the quantum yield (electrophotographic sensitivity) by sensitising the internal photoeffect (spectral, structural, and injection) are analysed for linear polymers with saturated and conjugate bonds and polymeric charge-transfer complexes.
The nature of the phenomena underlying the photogeneration of free charge carriers in the class of substances under consideration is discussed. It is shown that the maximum electric fields under electrophotographic conditions ensure the attainment of the maximum quantum yield and correspondingly the maximum light sensitivity compared with other applications of organic semiconductors in photographic processes. The bibliography includes 97 references.

CONTENTS

I.	Introduction	596
II.	Structural characteristics and electronic spectra of linear polymers	597
III.	Structural sensitisation of the electrophotographic response	604
IV.	Spectral sensitisation of the electrophotographic response	608
V.	Injection sensitisation of the electrophotographic response	610
VI.	The quantum yield and the structure of polymers	611

I. INTRODUCTION

The development of methods for the optical recording of information and of means for its storage and processing as well as coherent optics requires the development of photographic processes with new characteristics, which are frequently in principle unobtainable in classical photochemical processes (treatment in a realistic time interval, the possibility of repeated recording of information, etc. as well as economic characteristics).

One of the new photophysical processes with the required characteristics is electrophotography (EP) based on the phenomenon of the photoeffect in electrically charged high-resistance films. Organic polymeric photoconductors are a promising class of materials for the formation of EP media. The combination of thermal stability and effective mechanical and other specific properties of polymers with those of photoconductors suggests that they will be widely used in the future as a basis for the creation of new photographic processes. Polymeric photoconductors possess technically important properties such as optical transparency, capacity for forming films, flexibility, and thermoplasticity and ensure that the appropriate layers can be readily manufactured on a technological scale at a low cost. The attractive possibility of synthesising photoconductors and particularly polymers with specified properties by methods of organic chemistry also initiated a vigorous development of research on these substances.

Studies on the possibility of manufacturing EP and other silver-free layers on the basis of polymeric photoconductors are being prosecuted at the present time in the USSR, the USA, Poland, Japan, German Federal Republic, and other countries and definite successes have been achieved in this field. Information about the applications and properties of organic photoconductors which are in principle suitable for EP processes can be found in a number of publications [1-6]. We shall only note that molecular organic compounds of a wide variety of classes, particularly anthracene and its substituted derivatives, pyrene, aryl-, diaryl-, and triaryl-amines, triaylmethane dyes and their leuco-bases, tetraarylmethanes, derivatives of furan and thiophen, pyrazolines, phthalocyanines, vinyl derivatives of heterocyclic compounds, organometallic compounds, polymeric compounds, polyacetylenes, polyvinylanthracene, polyacrylamide, modified poly(vinyl chloride), polyselenomethylene, and many others are used as light sensitive media. Numerous studies have been devoted to the use in electrophotography of poly-*N*-vinylcarbazole and other polymers containing in their structure the carbazole ring system, for example, polyallylcarbazole, polypropenylcarbazole, and poly-*N*-acryloylcarbazole and their derivatives, polymers and copolymers based on 1,4-divinylcarbazole, as well as polymers based on polyvinylcarbazole with amino-, nitro-, and halogeno-substituents introduced into the aromatic ring.

However, the problem of the relation between the magnitude and spectrum of the photosensitivity, on the one hand, and the structure of polymers, on the other, and of the limiting possibilities, particularly the limiting light sensitivity of photographic processes in organic polymers, still remains obscure. Nevertheless, interest in the study of these problems is associated not only with the possibility of improving considerably the parameters of the existing silver-free photographic processes but also with the possibility of discovering new promising principles for achieving such processes. The solution of these problems involves considerable difficulties, related not only to the usually low light sensitivity of polymeric structures but also to the extremely limited number of film-forming substances which can be used to create thin homogeneous photosensitive films.

In the present review an attempt is made to examine the relation between the quantum yield of the internal photoeffect and the structure of linear polymers and to investigate the possibility of increasing the quantum yield (EP-sensitivity) by sensitising the internal photoeffect (photoconductivity). Polymers with saturated and conjugated bonds and polymeric charge-transfer complexes

are examined from this standpoint and the possibility of their structural, injection, and spectral sensitisation is analysed. The aim of the present review is not to cover fully all the existing studies; furthermore, only those publications have been selected which contain data on the molecular and supermolecular structures.

II. STRUCTURAL CHARACTERISTICS AND ELECTRONIC SPECTRA OF LINEAR POLYMERS

In contrast to the π and σ electrons localised between two nuclei in saturated systems, the π electrons in compounds with a polyconjugation system belong to the entire conjugated section of the molecule as a whole, which leads to a different distribution of molecular energy levels. A relation between the position of the absorption band and the length of the polyene system has been established[7]. Theoretical examination of the spectra of infinite polymers with a conjugated system has shown that, when the length of the conjugated section $n_c \to \infty$, the distance between the ground and excited electronic levels $\Delta E \neq 0$.[8-10] In polyenes states with alternating single and double bonds are energetically more favourable. The absence of a bathochromic shift of the spectrum with increase of the degree of polymerisation n_p can therefore indicate both that $n_c \ll n_p$ and that initially the conjugated chain length n_c is the same as n_p when the degree of polymerisation increases, after which the bathochromic shift ceases[11]. According to estimates by different workers, ΔE is in the range 0.5–2.0 eV.

1. POLYMERS WITH SATURATED CARBON–CARBON BONDS IN THE MAIN CHAIN

The electronic absorption and reflection spectra in the vacuum ultraviolet region have been studied for a wide range of light-sensitive organic polymers with different molecular structures: vinyl polymers with functional groups; copolymers based on them; vinyl polymers containing aromatic substituents in a side chain; polymers with conjugated bonds in the main chain and with aromatic substituents; polymers containing aromatic rings as elements of the main chain[12-22].

The reflection spectra of vinyl polymers with different functional groups and copolymers based on them consist of a series of overlapping bands with individual maxima for each polymer (Fig. 1*a*). The spectrum of polyacrylonitrile (curve *1*) shows distinctly a band with a broad diffuse maximum at 115–140 nm and a maximum in the region of 100 nm. The reflection spectra of copolymers based on vinyl chloride consist of two bands with maxima near 90–100 nm and 145–155 nm. The reflection spectra of polymers containing benzene rings (Fig. 1*b*) consist of two bands: a short-wavelength band in the range 50–150 nm and a long-wavelength band in the range 150–250 nm. The band structure is specific to each polymer, but all the spectra show maxima near 195 and 90–100 nm. A decrease of temperature to 170 K (Fig. 1*a*) leads to the splitting of the maxima and a narrowing of the bands[13]. Thus maxima at 110, 137, 150, 184, and 210 nm are clearly seen for polyacrylonitrile; when the temperature is reduced, each of the two maxima of poly(vinyl chloride) is apparently split in two: the first has peaks at 97 and 110 nm and the second at 125 and 143 nm and a new maximum appears at 210 nm.

It has been shown[15] in relation to polystyrene that the reflection and absorption spectra in the vacuum ultraviolet region coincide. In relation to the absorption spectra of polymers with saturated bonds, the molecular exciton theory, based on the hypothesis that the bonds in the ground state do not interact and that there is a dipole–dipole interaction between them on excitation, predict a quasi-continuum[23]. The presence of absorption bands with distinct maxima in the spectra, the high photoconductivity quantum yield, reaching unity[24], and the correspondence between the positions of the absorption maxima in the spectral region associated with the ionisation of the monomeric unit [115 nm for poly(vinyl chloride) and 104 and 127 nm for polyacrylonitrile][25] makes it possible to relate the nature of the absorption by these polymers to the ionisation of the corresponding monomeric unit.

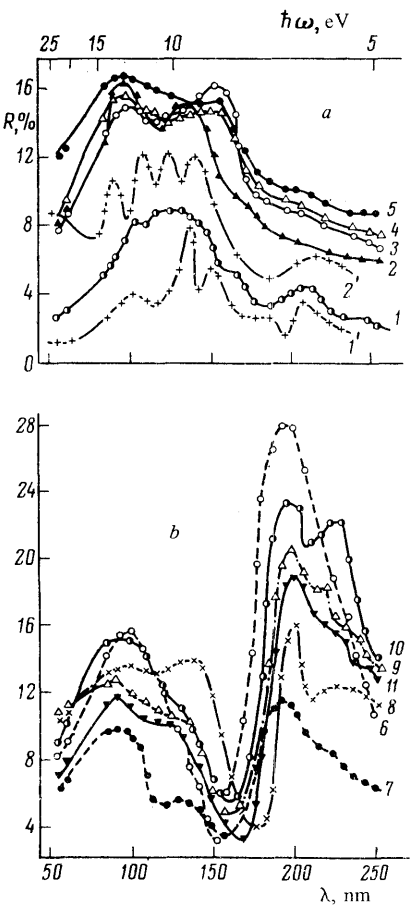


Figure 1. The reflection spectra of organic polymers with functional groups (*a*) and benzene rings (*b*)[13,14]: 1) polyacrylonitrile; 2) poly(vinyl chloride) [1^1) and 2^1) at 170 K]; vinyl chloride–vinylidene chloride copolymer; 4) vinyl chloride–vinyl acetate copolymer; 5) vinyl chloride–methacrylate copolymer; 6) polystyrene; 7) styrene–acrylonitrile copolymer; 8) styrene–2-ethylhexyl acrylate copolymer; 9) polytolane; 10) styrene–polytolane copolymer; 11) polycarbonate.

The presence in the reflection spectra of polymers containing benzene rings of maxima at 195 and 90–100 nm, characteristic of the excitation (195 nm) and ionisation (95 nm) [25] of benzene, suggest that the mechanism of light absorption by these polymers is determined by the properties of the benzene ring. Indeed the electron density of the monomer unit may shift towards the benzene ring in polymers containing benzene rings as elements of the main chain or side groups [26]. The nature of the absorption spectra of such polymers is then apparently determined by the properties of the benzene ring perturbed by the remaining atoms of the monomeric unit. In the 180–250 nm region of the spectrum (long-wavelength band), the π electrons of the benzene ring are responsible for the absorption [27], while in the short-wavelength region two excitation mechanisms probably operate: based on the π electrons and σ electrons of the bonds in the benzene ring. The latter process may be accompanied by the abstraction of a proton, since the energy of the C_6H_5–H δ bond is 12.6 eV (98 nm). [25]

The the absorption spectrum of vinyl polymers with different functional groups in the region 5–23.1 eV is determined by the properties of the monomeric unit and not the isolated bonds. The absorption spectra of polymers containing benzene rings either in the main chain or as side groups are determined by the properties of the benzene ring perturbed by the remaining atoms in the monomeric unit.

The low-temperature effect involving an "enhancement of the structure" of the absorption spectra [13] is associated with the vibrational excitation processes involving the molecules of a solid having a molecular structure. This effect can probably serve as direct proof of the significant role of vibrational excitation in making the structure of the energy spectra of photoelectrons less definite at 293 K for a number of aromatic crystals in the range 6–14.5 eV, which was observed by Zagrubskii and Vilesov [28]. The diffuse nature of the photoelectron spectra (this is also pointed out by Zagrubskii and Vilesov [28]) cannot serve as adequate evidence for the presence in the organic semiconductors of broad filled bands. Although Geacintov and Pope [29] showed by an analysis of literature data that the theory developed for indirect transitions in inorganic substances [30,31] is applicable to organic solids with a molecular structure (anthracene, tetracene), the idea of a continuous distribution of electrons with respect to energies in a molecular crystal is physically unjustified. The low mobility of charge carriers and the agreement between the absorption spectra of the crystal and the free molecule shows that the energy bands in these substances are very narrow [30–33].

On excitation with ultraviolet radiation, polymers of the vinyl series exhibit a universal luminescence in the range 70–400 nm, which depends strongly on the chemical structure, the degree of polymerisation, the degree of cross-linking of the polymer chains, the state of aggregation, and temperature, while on excitation with vacuum ultraviolet radiation the luminescence quantum yield depends on the wavelength of the exciting radiation [19,34–40].

2. POLYMERS WITH CONJUGATED CARBON–CARBON BONDS IN THE MAIN CHAIN

Since the chain in the polymer is non-planar and the degree of overlap of the π-electron orbitals depends on the angle of rotation about a single bond, it follows that, in all cases where the size of the conjugation block or the degree of conjugation in the block n_c are considered and compared with planar polyene reference systems, one is dealing with an effective conjugation where the size of the conjugation region n_c is not equal to the number of units in the block n_p. The effective conjugation is usually determined by comparing the positions of the maxima in the optical spectra of the polymer investigated and reference systems having a planar polyene chain [11].

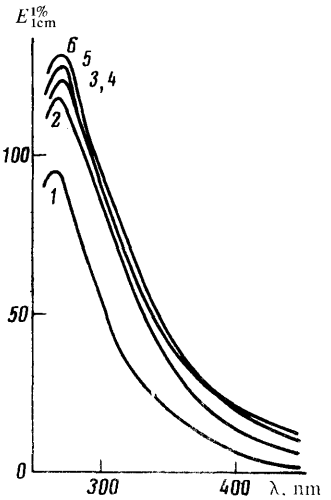


Figure 2. Absorption spectra of polychlorocyclopentene (solution in benzene) [11] for different molecular weights: 1) 450; 2) 1075; 3) 2450; 4) 3000; 5) 3660; 6) 4220 ($E^{1\%}_{1\,cm}$ optical density of 1% solutions for a cuvette 1 cm thick).

(a) Polymers with Double Bonds (Polyene Chain)

Poly-3-chlorocyclopent-1-ene (PCCP). An increase of the molecular weight (M) of the low-molecular-weight fraction entails an increase in the absorption intensity in the long-wavelength part of the spectrum [11] (Fig.2). The spectra of molecular fractions are very similar and the position of the maximum (270–274 nm) does not change from fraction to fraction and shows that small conjugated regions, embracing three units of the micromolecule (there are sections containing up to seven double bonds) predominate.

(b) Polymers with Aromatic Substituents [11]

Polyphenylacetylene, whose structure contains polymeric aromatic PPAT-150 conjugation blocks (phenylacetylene polymer obtained at 150°C) together with polyene units, has conjugation regions with an average length n_c, which is not the same as the length of the molecule and is smaller than the length of the lowest-molecular-weight fraction, i.e. $n_c \leq n_p = 8$. Treatment of PPAT-150 at 300°C (PPAT-150-300) results in an increase of absorption, although the molecular weight of the polymer

decreases (Fig. 3*a*). Comparison of the spectra of the PPAT-150 and PPAT-150-300 fractions leads to the conclusion that the average lengths of the conjugation regions in these polymers is smaller than the length of the units of the lowest-molecular-weight fraction, i.e. $n_C \leq 5$. Since the extinction coefficient ϵ is related to the optical density by the expression $\epsilon = E^{1\%}_{1\,cm} \times M/10$, where M is the molecular weight and $E^{1\%}_{1\,cm}$ the optical density of 1% solutions for an optical path length in the cuvette of 1 cm, it is found to be proportional to M of the fraction at the same wavelengths and the number of absorbing centres increases with increase of M of the polymer. The dimensions of the absorbing centre incorporate a region smaller than the length of the polymer chain.

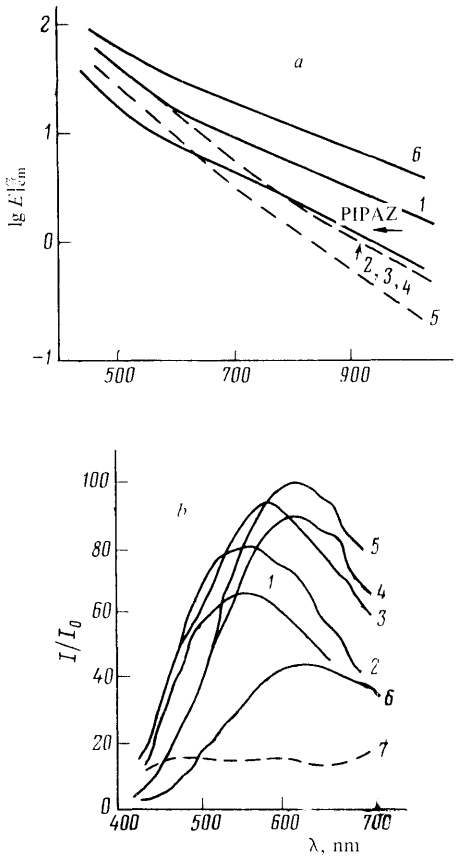


Figure 3. Absorption (*a*) and luminescence (*b*) spectra of polyphenylacetylene [11]: *a*) [1) PPAT-150 (790); 1′) PPAT-150 (1370); 2) PPAT-150-300 (500), PPAZ (2900); 3′) PPAZ-760; 4) PPAT-300 (760); 5) PPAT-400 (300); 6) PPAT-150-400 (650)]; *b*) [1) PPAT-150 (1060); 2) PPAT-150 (1590); 3) PPAT-150 (800); 4) PPAT-150 (1310); 5) PPAT-150 (1340); 6) PPAT-150 (1510); 7) PPAT-150 (2160); 8) PPAT-150 (1200); 9) PPAZ (1020); 10) PPAZ (2900); 11) PPAZ (5300); 12) PPAZ (7600)]. Here and henceforth the numbers in round brackets are the molecular weights M and the numbers in front of the brackets represent the polymerisation or heat treatment temperature (°C). The luminescence spectra are given in relative equienergetic units (I/I_0).

The average length of the PPAZ conjugation region [phenylacetylene polymer obtained in the presence of the $(C_2H_5)_3AlTiCl_3$ catalyst] proves to be greater than for PPAT-150 and PPAT-150-300, but smaller than for PPAT-300. Despite the fact that the average number of polymer units in PPAZ is 70–80, the average length of the conjugation region does not exceed the length of the conjugation region in PPAT-300, i.e. $n_C < 8$. Since the absorption of PPAZ is weaker than that of PPAT-300, it is difficult to suppose that the absence of a bathochromic shift of the PPAZ absorption spectrum is associated with the attainment of the equality $n_C - n_p$. PPAC apparently consists of individual short conjugation regions [11]. The spectra of the PPAT-150-400 fractions have a different form. Here there is a distinct increase of absorption intensity in the long-wavelength region with increase of M of the polymer. The increase of absorption intensity in the region of long wavelengths with increase of the temperature of the synthesis or heat treatment corresponds to the formation of longer conjugation regions. At the same time the average length of the polymer chain decreases. The average length of the conjugation region in PPAT-150-400 now includes the entire macromolecule. The value of M shows that PPAT-150-400 cannot have a value of n_C greater than 3–7. Comparison with the spectra of polyenes shows that the average length of the conjugation region does not exceed 5–6 for PPAT and 7–8 for PPAZ.

The luminescence spectra of PPAT [11] consist of a family of similar curves whose maxima are located at similar wavelengths (580–660 nm) with certain differences in the structure and intensity of the lines (Fig. 3*b*). It had been established earlier that similar changes in the spectra, characterised by a redistribution of the intensities in their fine structure, are observed when M (chain length) and polymer structure are altered, being particularly pronounced for chain molecules with a conjugation system [41]. Hence it follows that identical, within certain limits, positions of the maxima in the luminescence spectra are characterised by the same effective conjugation n_C. Assuming that the positions of the maxima in the luminescence spectra of PPAT and polyene chains are the same, one can conclude that the PPAT-150 fractions contain conjugation blocks with $n_C = 5–6$. This follows from a comparison of the PPAT spectra with the spectra of diphenylpolyenes both in solution and in the solid state. The average position of the maximum in the luminescence spectra of the PPAT-150 fractions is at ~620 nm, i.e. in the region between the maxima of diphenylhexatriene (530 nm) and diphenyloctatetraene (670 nm). One can therefore suppose that the conjugated chains of the PPAT-150 fraction have luminescence characteristics identical with those of a compound having intermediate properties.

The fact that the spectra of different fractions have different structures with some variation in the position of the maximum (which should not happen if the continuous conjugation sections contain identical numbers of units) confirms that the fractions contain in their chains different combinations consisting mainly of blocks with $n_C = 5$ and 6. The luminescence spectra of such polymer chains, in which regions with the larger value of n_C predominate in the solid state, should exhibit a lower intensity and the band maxima should be displaced towards longer wavelengths as a result of a redistribution of intensities in the individual bands of the fine structure of the spectrum. When regions with the lower value of n_C predominate, the opposite rearrangement of the structure of the absorption spectrum should occur. The statistical contribution of

regions with $n_C < 6$ and $n_C < 5$ is very insignificant: they are not observed in the spectra. Conjugation regions with $n_C > 6$ cannot actually be manifested in the spectrum owing to the low intensity of their luminescence in the solid polymer and the small number of such regions. On the other hand, regions with $n_C = 4$, the luminescence intensity of which in the solid state exceeds that observed for the conjugated regions with $n_C = 5$ by a factor of ~10, should appreciably increase the luminescence intensity of the spectrum in the region of 440 nm even when their content in the chain is low. However, the luminescence of the polymer in this region is insignificant, so that one may conclude that the number of conjugate regions with $n_C = 4$ in the overall balance is extremely small. The spectra of the PPAT fractions 6 and 8 (Fig. 3) characterise chains made up of individual conjugated regions with $n_C = 5$ and 6. In terms of the relative luminescence yields of these regions, their ratio in the above fractions can be estimated as 1 : 7.

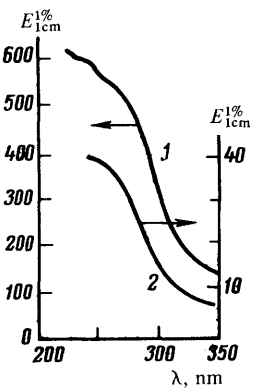


Figure 4. Absorption spectra of polymethylethynylpyridine (curve *1*) and polyphenylacetylene (curve *2*).[11]

With increase of M, the maximum in the luminescence spectra of PPAZ is steadily displaced towards longer wavelengths and the intensity falls sharply[11,41,42]. This change in the spectrum shows that M and the conjugation increase in parallel. PPAZ differs markedly from PPAT by a higher molecular weight M and a more extensive continuous conjugation. Analysis of the spectra shows that the chains in all the fractions of this polymer consist of different combinations of regions with $n_C = 6$–9. The markedly diffuse nature of the maxima in the spectra of all the fractions indicates a broad statistical distribution in terms of the extent of conjugation. All the fractions should therefore contain the regions with all the continuous conjugations enumerated above in the appropriate proportions. The PPAZ fraction 5 contains predominantly regions with $n_C = 6$ and 7, conjugation regions with $n_C = 7$ predominate in the PPAZ fraction 6, while regions with $n_C = 8$ predominate in the PPAZ fraction 8.

Polymethylethynylpyridine (PMEP) [11] does not differ from PPAT as regards the principle underlying the structure of the macrochain and the earlier conclusions are valid also for it. The electronic spectra of PMEP and PPAT (Fig. 4) do not show significant differences, particularly in the region of 300 nm, and consist of curves without appreciable maxima, which decrease in the direction of longer wavelengths; the absorption in the visible region is insignificant. It appears that the continuous conjugation extends to regions with $n_C = 3$–5.

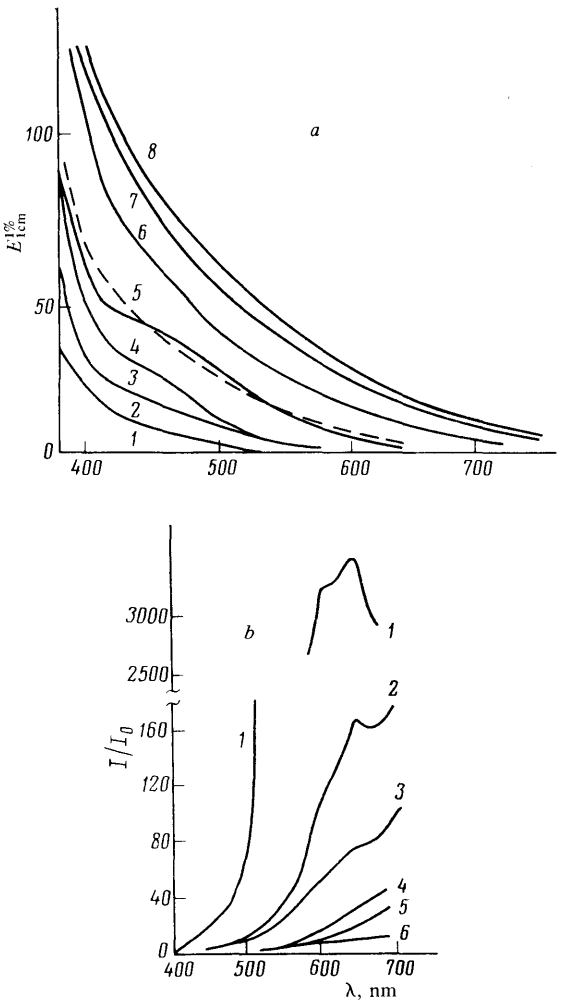


Figure 5. Absorptions (*a*) and luminescence (*b*) spectra of polydiphenylacetylene [11]: *a*) [1) 400 (406); 2) 300 (675); 3) 300 (830); 4) 300 (920); 5) 350 (1060); 6) 400 (860); 7) 400 (950); 8) 400 (660)]; *b*) [1) 300 (850); 2) 300 (850); 3) 350 (1060); 4) 400 (660); 5) 400 (930); 6) 400 (1200)].

(c) Polymers with Two Aromatic Substituents

Polydiphenylacetylene (PDPA) consists of a linear polymer whose structure contains a system of conjugated bonds and aromatic side groups which stabilise the main polyene chain of the macromolecule[43]; the end groups consist of hydrogen atoms. An increase of M induces a bathochromic shift of the absorption band (Fig. 5*a*), i.e. the length of the conjugation region is comparable to the

length of the macromolecular chain. However, an increase of polymerisation temperature causes an even greater shift for the same value of M (curves 6 and 9), which is apparently due to the inclusion of benzene rings in the conjugation chain.

The luminescence spectra of PDPA [11,44] (Fig. 5*b*) are analogous to those of PPAT and PPAZ. The position of the PDPA-300 (polymer obtained at 300°C) luminescence maximum shows that these polymers are characterised by $n_C = 6$ with some proportion of regions with $n_C = 7$ and an insignificant content of regions with $n_C = 5$. Since PDPA-300-6 and PDPA-300-10 (polymerisation times 6 and 10 h respectively) have molecular weights of 850 and 930 respectively, while $M = 180$ for the monomeric unit, the PDPA-300-6 chains are continuously conjugated over the entire length of the system; the benzene rings are then included in the conjugation chain. The high intensity of the luminescence of PDPA-300-6 is comparable to the intensity of the luminescence of special technical phosphors.

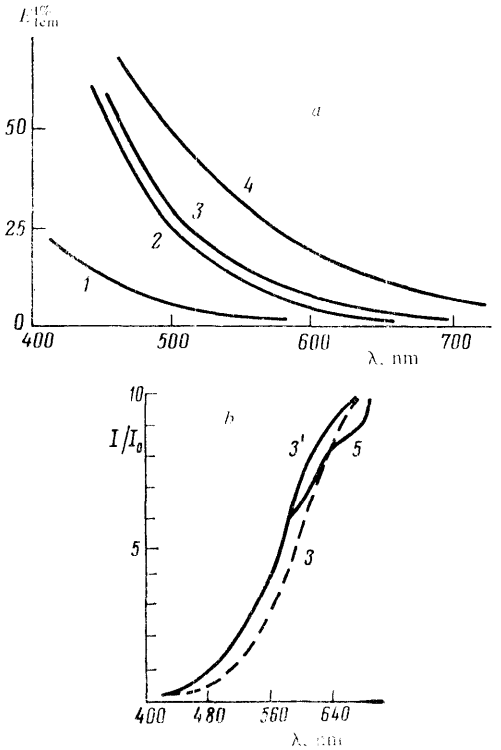


Figure 6. Absorption (*a*) and luminescence (*b*) spectra of polydiphenylbutadiyne [11]: *a*) [1) (1080); 2) (1450); 3) (3500); 4) product of the heat treatment of the non-fractionated polymer at 400°C ($M = 2100$)]; *b*) [3) (940); 3′) (2000); 5) (2120)].

(d) Polymers with a Binary Conjugation System (Acene Structures) [11,44]

Polydiphenylbutadiyne (PDPB). A change in M by a factor greater than 2 (from 1450 to 3500) does not entail a significant change in the spectrum (Fig. 6*a*). On this basis, it is suggested that the degree of continuous conjugation n_C in PDPB is constant and does not agree with the length of the macromolecule. Heat treatment of the polymer at 400°C is accompanied by an appreciable increase of absorption intensity in the long-wavelength region of the spectrum. The increase of the conjugation block on heat treatment can be associated primarily with the additional cyclisation of the polyene fragments. Furthermore, heat treatment promotes a coplanar arrangement of sections of the macromolecule which had been rotated in different ways prior to this and also a decrease of strain within the cyclic regions of the chain and the inclusion in the conjugation chain of some of the benzene rings in the side groups. However, within certain limits the positions of the bands in the luminescence spectra characterise the same values $n_C = 6$ and 7 (Fig. 6*b*).

Optically homogeneous films can be obtained from PDPB by vacuum vaporisation [44]. In a vacuum of 10^{-5}–10^{-6} mmHg at a melt temperature of 500°C, a rate of deposition of the layer not exceeding 0.05 μm min^{-1}, and a temperature of the surface (support) in which the vapour is condensed up to 450°C, optically homogeneous layers are obtained, greatly exceeding in terms of this parameter layers prepared by casting from solution [44]. Vacuum sputtering increases appreciably the optical density of the layer compared with the layers obtained from solution (Fig. 7). A determination of the average molecular weight of the PPAZ decomposition products [45] suggests that the PDPB molecule is broken up during vacuum sputtering at the weakest sites in the chain into blocks consisting of several units.

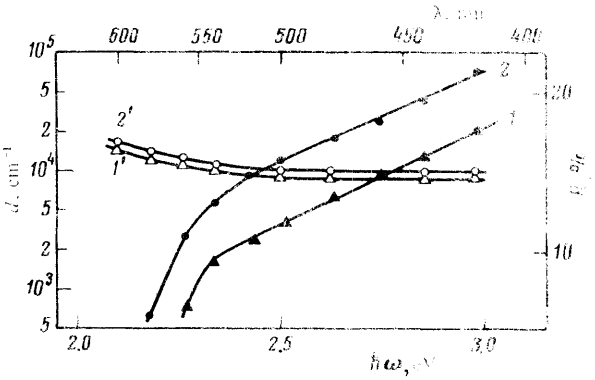


Figure 7. Absorption (curves 1 and 2) and reflection (curves 1′ and 2′) spectra of polydiphenylbutadiyne films obtained from solution (curves 1 and 1′) and by evaporation in a high vacuum (curves 2 and 2′). [44]

Poly-β-iodophenylacetylene. β-Iodophenylacetylene polymers obtained by thermal polymerisation (PIPAT) and polymerisation in the presence of Ziegler–Natta catalysts (PIPAZ) exhibit an appreciable absorption in the visible and ultraviolet regions characteristic of conjugated systems [11] (Fig. 8*a*). In the red and near infrared regions the absorption of PIPAT is stronger than that of PIPAZ. In the blue-violet region their absorptions are approximately the same. There is no structure whatever in the spectrum and the latter is markedly diffuse.

The continuous conjugation extends over regions which are small compared with the length of the molecule. The low value of $E^{1\%}_{1\,cm}$ shows that the fraction of molecules with long conjugation regions is small.

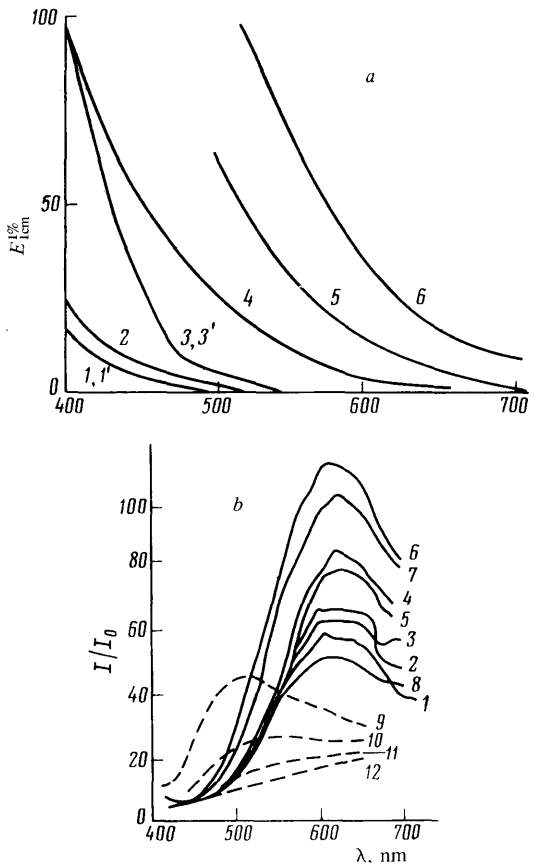


Figure 8. Absorption (*a*) and luminescence (*b*) spectra of polyiodophenylacetylene[11]: 1) (1300); 2) (1000); 3) (1770); 4) (2200); 5) (870); 6) (2400); 7) iodophenylacetylene (IPA) dimer with M = 456, PIPAZ (1680).

Bearing in mind that the different substitutions of side groups by other groups in simple carbon–carbon chains leads to an alteration of the structure of the spectra the extent of which is much smaller than the change in the position of the maximum caused by the difference in the degree of continuous conjugation in the chain[41], and despite the possible influence of iodine, one can estimate approximately the structure of the chains. Thus fractions *1* and *2* contain blocks with n_C = 6 and n_C = 6 and 7 respectively; fraction *3* contains regions with n_C = 7 and to a small extent n_C = 6; fractions *4* and *6* consist predominantly of regions with n_C = 7 and 8. Comparison of the molecular weights and the sizes of the conjugation region shows that in this instance continuous conjugation does not apparently embrace the entire macromolecule and individual conjugation blocks exist.

3. POLYMERS WITH CONJUGATED CARBON–NITROGEN BONDS IN THE MAIN CHAIN

Polymers with conjugated carbon–nitrogen multiple bonds, the so-called poly-Schiff bases[45,47], are organic polymers which contain in the main chains systems of conjugated >C=C< and >C=N– bonds as well as nitrogen atoms containing in the outer energy level electrons which are not involved in chemical binding. Poly-Schiff bases are synthesised[48,49] by the polycondensation of diamines (*p*-phenylenediamine, *m*-phenylenediamine, and benzidine) with dicarbonyl compounds (benzil) using an excess of one of the bifunctional compounds.

The influence of the molecular and supermolecular structures on the optical and photoelectric properties was studied for three types of compounds: (I) initial poly-Schiff bases; (II) hydrogenated polymers; (III) block-copolymers[50].

The initial polymers, obtained from *p*-phenylenediamine and benzil using an excess of the diamine or benzil, from *m*-phenylenediamine and benzil, and from benzidine and benzil, consist of coloured powders. The hydrogenated polymers are amorphous powders with a lighter colour than the corresponding initial polymers. The absence of degradation in the course of hydrogenation was confirmed by measurements of the molecular weights of the polymers and by infrared spectroscopy. The softening temperature of the hydrogenated polymers is reduced and their solubility is improved somewhat. The block-copolymers can be divided into two groups[48,49]. The first group includes products of the combination of dicarbonyl polyconjugated blocks with diamines. These copolymers have a lighter colour and are more soluble in dimethylformamide than the initial polymers. The comparatively low viscosities, high softening temperatures, and low solubilities of the products of the coupling of the blocks to one another are apparently due to the strong interaction between the polyconjugated blocks of different chains and the limited mobility of the blocks when they are incorporated in a polymer chain[51]. The second group of block copolymers are products of the coupling of polyconjugated blocks containing terminal amino-groups to flexible poly(ethylene glycol) blocks. With increase of the length of the flexible block, the interaction between flexible blocks and between polyconjugated blocks diminishes in this group. It is noteworthy that, by virtue of the above factors, those copolymers lose their capacity for crystallisation (they are amorphous).

In molecules with conjugated bonds containing heteroatoms, the lone electron pair of nitrogen is conjugated with the π electrons of the conjugated bond[46] and this so-called n,π conjugation, which influences the molecular geometry, obtains in addition to the π,π conjugation. The polyconjugated systems considered do not therefore constitute a single conjugation system and are made up of a collection of sections with delocalisation of electron density. The weakening of the delocalisation of electrons along the conjugation chain can occur as a result of the displacement of the system from coplanarity, the introduction of a benzidine group and *meta*-substituted benzene rings, and hydrogenation. This result is confirmed by the nature of the electronic absorption spectra. Thus the spectra (Fig. 9, curves *4–6*) clearly reveal the disappearance on hydrogenation of the long-wavelength maxima corresponding to the conjugation system (the signal characteristic of polymers with a conjugation system disappears from the EPR spectra of the hydrogenated polymers). An increase of molecular weight also weakens the

delocalisation of electrons. In the series of polymers with M = 600, 1000, and 1330 (Fig. 9) the maximum is displaced towards shorter wavelengths, from 372 to 350 nm, which indicates the occurrence of this effect.

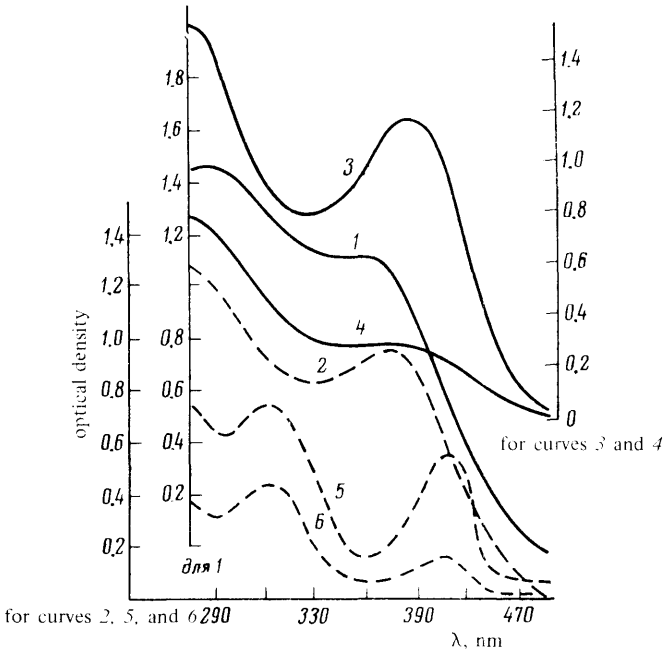


Figure 9. Absorption spectra of poly-Schiff bases with different molecular weights [1) 1330; 2) 1000; 3) 600] and hydrogenated specimens (curves 4–6).[50]

4. POLYMERIC CHARGE-TRANSFER COMPLEXES

Polymeric charge-transfer complexes (CTC) have been recently examined in a review[2]. In CTC the generation of photocarriers is associated with charge transfer from the donor to the acceptor in the molecules of the complex, accompanied by the liberation of the charge-transfer energy $E_{ct} = I - E_A - E_c$, where I is the ionisation potential of the donor, E_A the electron affinity of the acceptor, and E_c the energy of the Coulombic interaction between the ions A and D.[52] The generation of the charge carrier can be described by the following equation:

$$(D \ldots A \leftrightarrow D^+ \ldots A^-) \overset{h\omega, ct}{\rightleftarrows} (D^+ \ldots A^- \leftrightarrow D \ldots A),$$

so that in the excited state the equilibrium is displaced towards the ionic form.

To a first approximation photoexcitation (or the charge-transfer energy) depends on the two quantities I and E_A and, when I = const., E_{ct} can be reduced as a result of an increase of E_A, which is equivalent to a bathochromic shift of the absorption band[53,54]. It is noteworthy that in the general case there is no correlation between the electron affinity of the acceptor in polyvinylcarbazole (PVC) complexes and the photoconductivity of the CTC for acceptors of different classes. Such correlation occurs only for acceptors with similar π-electron clouds and the relative dimensions of the donor and the acceptor can apparently play an appreciable role in this process[55–57].

(a) The Similarity of the Electronic Natures of Organic High- and Low-Molecular-Weight Photoconductors

In polymers with a conjugation system, for example in PPA, PDPA, PDPB, etc., continuous conjugation does not embrace the entire macromolecule and consists of individual conjugation sections (blocks), so that the size of the macromolecule greatly exceeds the size of the average conjugation block. The conjugation between blocks is to a large extent weakened owing to their non-coplanarity. The mechanism of the formation of conjugation blocks in the polymerisation of compounds of the acetylene series is associated with the dependence of the electronic transition energy ΔE_π on the number of π electrons.[11] Fig. 10 illustrates the dependence of ΔE_π on the number of π electrons (N_π) for α,ω-diphenylpolyenes and polyacenes.[58] Whereas in α,ω-diphenylpolyenes containing conjugated double bonds there is a tendency towards a limit and, when $n > 5$, the quantity $\Delta E \to 2.5$ eV [$\Delta E = 2.5$ for the system R(–HC=CH–)$_n$R, where R = CH_3 and $n = 15$ [58]], in acene systems with a slight alternation of bonds ΔE_π decreases fairly rapidly with increase of N_π and there is only a slight tendency towards a limit. The results obtained from electronic absorption spectra are confirmed by theoretical calculations by the Hückel method. For α,ω-dimethylpolyenes containing conjugated double bonds, the calculated limiting value is $\Delta E = 2.25$ eV.[59]

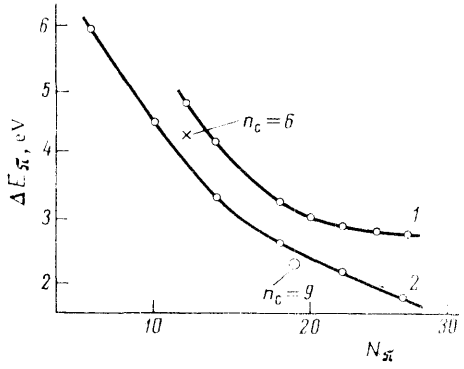


Figure 10. Dependence of the electronic transition energy ΔE_π on the number of π electrons for α,ω-diphenylpolyenes (curve 1) and acenes (curve 2). The crosses represent the activation energies for conduction in polymers with different conjugation blocks: $n_c = 6$ for PPAT, $n_c = 9$ for PPAZ and PDPB.[11]

Thus experimental data and quantum-chemical calculations show that the energy gain in diphenylpolyenes in the optical transition changes insignificantly on successive increase of the conjugation blocks and gradually tends to zero when ΔE_π approaches 2.5 eV. For definite value of

n, a non-coplanar addition of the $(n + 1)$th unit is thermodynamically favourable, which leads to the formation of a new conjugation block non-coplanar with the preceding block. Analogous conclusions are valid for acene structures.

The data examined above suggest that the extent of π conjugation necessary for specific properties of polyconjugated polymers, including photoconductivity, does not exceed the extent of conjugation in low-molecular-weight organic compounds and the electronic structures of organic high- and low-molecular-weight substances are therefore the same.

III. STRUCTURAL SENSITISATION OF THE ELECTROPHOTOGRAPHIC RESPONSE

Electrophotography (EP) is based on the possibility of the formation in the material, when the latter is charged, of an electrical double layer made up of the surface charge and the shielding charge arising in the bulk phase or the conducting base, with subsequent local modulation of its power (the product of the charge density and the thickness of the double layer) as a result of photoconductivity. The drift of the charge carriers generated by light in the electric field of the double layer leads to the neutralisation of the surface charge or to a decrease of the thickness of the double layer.

The study of the problem of the non-photoactive absorption in molecular (polymeric) photoconductors under EP conditions led to the observation of the phenomenon of the so-called structural sensitisation of the photoeffect[60]. The phenomenon consists in the dependence of the spectrum and the quantum yield of the internal photoeffect on the molecular and supermolecular structures of the photoconductor. The nature of the molecular and supermolecular structures determines the probability of the generation of free charge carriers from the first bound state on absorption of a light quantum.

We shall consider this phenomenon in greater detail for polymeric photoconductors of different classes.

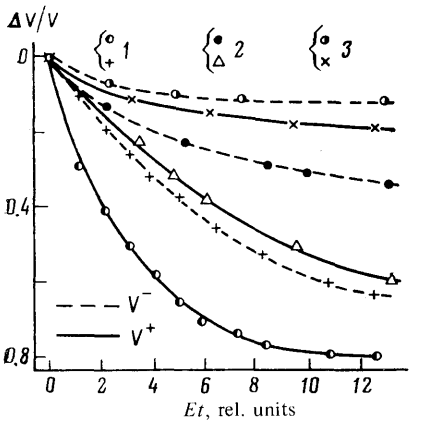


Figure 11. Monochromatic curves for the photodischarge of polystyrene EP layers (0.3 μm) [61]; λ (nm): 1) 115; 2) 147; 3) 180; Et = degree of illumination (relative units).

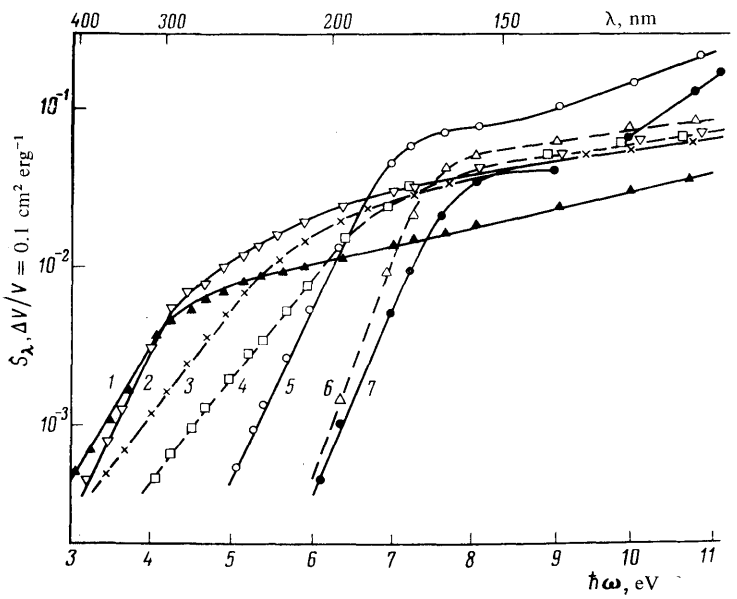


Figure 12. EP sensitivity spectra of polymer layers with saturated and conjugated bonds in the main chain constituting the basis of a catalogue of EP layers with a variable long-wavelength light sensitivity limit[61-64]: 1) polydiphenylbutadiyne; 2) polyvinylcarbazole; 3) polyphenylacetylene; 4) polyethylene; 5) polyacrylonitrile; poly(vinyl chloride); 7) polystyrene.

1. POLYMERS WITH SATURATED CARBON–CARBON BONDS

Among studies on the photoconductivity of polymers of the vinyl series with various functional groups[60-78], those devoted to the intrinsic photoconductivity occupy a special place. The phenomenon of the intrinsic photoconductivity of vinyl polymers in the vacuum ultraviolet region of the spectrum was observed in 1968 independently by two groups of investigators and was examined in two corresponding series of studies by Cherkasov and coworkers[60-65] and Ofran and coworkers[72-74].

Quantitative studies on the EP sensitivity spectra were carried out in the range 3–11 eV for polyethylene, poly(vinyl chloride), and polyacrylonitrile layers and in the range 3–21 eV for polystyrene layers[61-64]. The kinetics of the photodischarge of the EP layers based on the above polymers are characterised by curves which are asymmetric relative to the sign of the surface charge (Fig. 11). The shape of the curves depends on the wavelength: with increase of the latter, the rate of photodischarge decreases faster and the residual potential (the threshold value of the electric field for the non-photoactive absorption of light) increases. The nature of the EP sensitivity spectra of saturated polymers (as well as polymers with a polyconjugation system) in the vacuum ultraviolet region is approximately the same: the EP sensitivity depends on the sign of the surface charge and, for example, for polystyrene with a positive charge, it is greater by a factor of four than for the polymer with a negative charge. The dependence on the wavelength is more pronounced: for the same polystyrene, the EP sensitivity increases by a factor of 100–150 with decrease of wavelength by a factor of three (from 180 to 60 nm). The position of the long-wavelength limit of the EP sensitivity (Fig. 12) depends on the structure of the polymer and, for polymers of the vinyl series, is displaced towards longer wavelengths to an increasing extent in the presence of the following groups: benzene ring, chlorine, cyano-group, hydrogen, and the carbazole ring.

We may note that the above polymers (except polyethylene) are amorphous (vitreous). Polyethylene is crystalline, while polystyrene is atactic and isotactic and is capable of crystallising with a glass point at 95.5°C; poly(vinyl chloride) is atactic and has not been obtained in a crystalline form, its glass point being 80°C; polyacrylonitrile is atactic and has a flow temperature above the decomposition temperature; polyvinylcarbazole has a glass point of 117°C. In the above series the shift of the EP sensitivity limit is largely due to the shift of the absorption limit.

The study of the influence of the structure of the polymers with saturated bonds on the quantum efficiency showed (in relation to polystyrene)[61] that the latter is independent of the molecular weight in the range from 10^3 to 10^6. On the other hand, the number of double bonds in the main chain, which has been varied in a controlled manner by dehydrogenation, has a selective spectroscopic effect[61] (Fig. 13). Thus the quantum efficiency is constant in the range 120–135 nm, where valence electrons of the molecule are responsible for absorption, decreases in the range 135–180 nm with increase of the number of double bonds, and increases in the range 180–220 nm owing to the photoactive absorption by the C=C bonds of the main chain with their subsequent photodegradation accompanied by a decrease of the absorption in this part of the spectrum.

The above data on the energetic EP sensitivity of saturated polymers in the vacuum ultraviolet region made it possible for the first time to characterise quantitatively the photoconductivity phenomena and to determine in the first place the absolute quantum yield of the internal photoeffect.

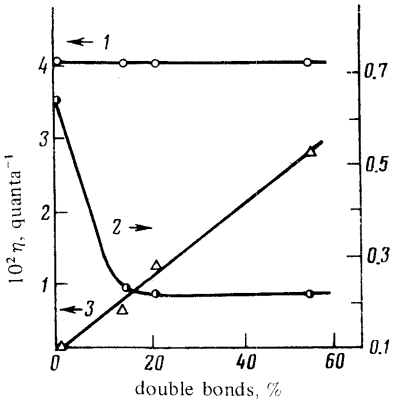


Figure 13. The selective spectroscopic effect of the change in the number of double bonds in the main chain of polystyrene on the EP sensitivity (quantum yield) of the layers[61]; $\Delta\lambda$ (nm): 1) 120–135; 2) 135–180; 3) 180–220.

Comparison of the sensitivity spectra of EP layers of polystyrene, EP layers of selenium, and photographic layers based on silver thiocyanate, developed specially for the vacuum ultraviolet region, showed[62,65] that the EP sensitivity of polystyrene layers exceeds that observed for silver thiocyanate layers and in the region of 60 nm approaches the sensitivity of selenium layers. The amount of light necessary to record the image (based on the criterion of the relative change in the potential of the EP layer $\Delta V/V = 0.1$) is 28 erg cm^{-2} at λ = 115 nm and 2.8 erg cm^{-2} at λ = 58.4 nm. The fairly high EP sensitivity of polymers of the given class in the vacuum ultraviolet region combined with a low sensitivity in the longer-wavelength part of the spectrum made it possible to reduce the background due to the scattered long-wavelength light in the recordings of images and led to the creation of a catalogue of EP layers for the vacuum ultraviolet region with a variable light sensitivity limit[66,68].

2. POLYMERS WITH CONJUGATED CARBON–CARBON BONDS

Polymers with a polyene chain (PCCP) do not exhibit EP sensitivity in the part of the spectrum under consideration, although they are charged to appreciable potentials.

For polymers with aromatic substituents (PPAT, PIPAT), the EP sensitivity and the limiting potential of the layers were found to depend on the supermolecular structure and on the presence of iodine atoms in the structure[64] (Fig. 14). Amorphous PPAT layers have a high limiting potential (both positive and negative), but their sensitivity is extremely low. The presence of iodine

atoms in PIPAT greatly reduces the limiting potential (to 5–10 V) but at the same time increases the EP sensitivity. The change of the supermolecular PPAZ structure from amorphous to crystalline (with a degree of crystallinity up to 80%) on slight decrease of the limiting potential leads to an appreciable increase of the EP sensitivity. The layers exhibit EP sensitivity in the <600 nm region of the spectrum with a maximum in the region of < 300 nm (Fig.15).

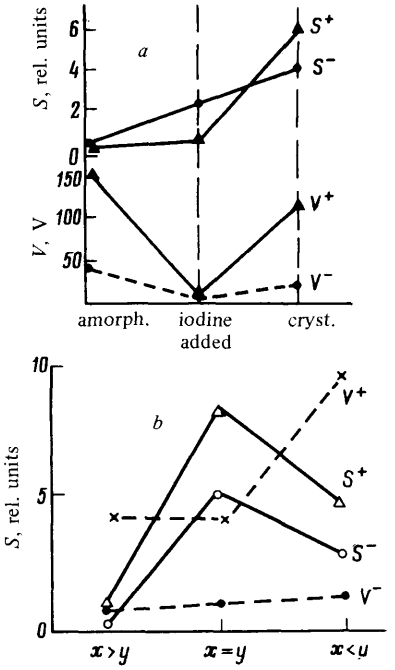
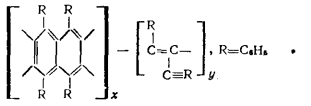


Figure 14. The influence of the structure of polymers on the EP properties of layers[64]; S—spectral sensitivity; V—limiting charging potential; *a*) polyphenylacetylene with a variable supermolecular structure and with the introduction of iodine atoms: PPAT (amorph.), PIPAT, PPAZ (cryst.); *b*) PDPB with a variable ratio of the initial components during synthesis:



The solvent has a marked influence on the EP parameters[60,64]. Aromatic solvents (toluene) are removed with much more difficulty from polymer films than solvents such as carbon tetrachloride. Thus CCl_4 is fully removed from the polymer film in the course of 4 h in a vacuum of 10^{-2} mmHg, while the complete removal of toluene requires a vacuum of 1×10^{-5} mmHg. Concentration and type of solvent do not affect the limiting potential of the EP polymer layers, but the presence of a solvent in the layer accelerates the dark relaxation of the positive potential in the polymer layers and to a greater extent at higher solvent concentrations (Fig. 16); on the other hand, the dark relaxation of the negative potential under these conditions remains almost unchanged. Rather thick (up to 10 μm) EP layers based on PPAZ, completely freed from the solvent, do not exhibit EP sensitivity in the ultraviolet and visible regions of the spectrum. The presence of a certain amount of solvent in polymer films leads to the appearance of EP sensitivity but only in positively charged PPAZ layers (Fig. 16). Thin (3 μm) PPAZ layers exhibit an appreciable EP sensitivity after the removal of the solvent (Fig. 16).

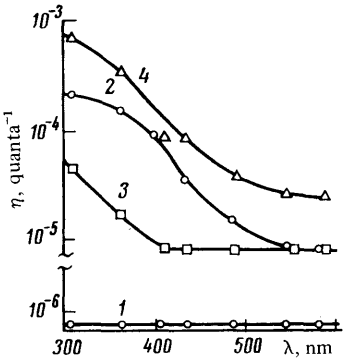


Figure 15. The spectrum of the quantum yield in layers of polyconjugated polymers[60]: 1) polychlorocyclopentene; 2) polyphenylacetylene; 3) polydiphenylacetylene; 4) polydiphenylbutadiyne.

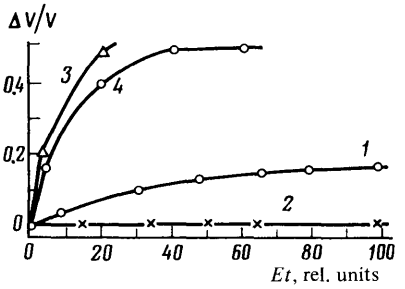


Figure 16. The retardation of the rate of photodischarge of EP layers following the removal of solvent (carbon tetrachloride) from polyphenylacetylene [64] (*Et* is the degree of illumination expressed in relative units): 1) and 3) initial layers [1) 11 μm; 3) 3 μm]; 2)–4) after the removal of the solvent.

EP layers based on polymethylethynylpyridine (PMEP) [11,64] are characterised by an asymmetry of the limiting potential and the kinetics of dark relaxation as well as the kinetics of photodischarge. The layers also exhibit a sensitivity only for a negative surface charge, which indicates the predominance of n-type charge carriers in the layers. The EP sensitivity is independent of the molecular weight and of the different types of treatment (polymers both soluble and insoluble in benzene have been isolated for a polymerisation temperature of 300°C).

The layers exhibit EP sensitivity in the ultraviolet part of the spectrum (< 400 nm); the sensitivity is then lower by an order of magnitude than for PPA layers (Fig. 15). The low EP sensitivity can be naturally accounted for by the high efficiency of the competing process—luminescence.

Polymers with a Double Conjugation System

The EP sensitivity of PDPB layers, obtained by casting from solution, depends on the ratio of x and y units in the structure (Fig. 14*b*). A common feature over the entire range of contents of the initial components is the asymmetry of the potential: the positive potential greatly exceeds the negative potential. The EP sensitivity varies in a complex manner: it is low for $x > y$, passes through a maximum at $x = y$, and decreases for $x < y$. The positive limiting potential then increases. The layers exhibit EP sensitivity over a wide spectral range (<600 nm) (Fig. 15) and have a broad maximum at 400–440 nm and a second maximum at shorter wavelengths.

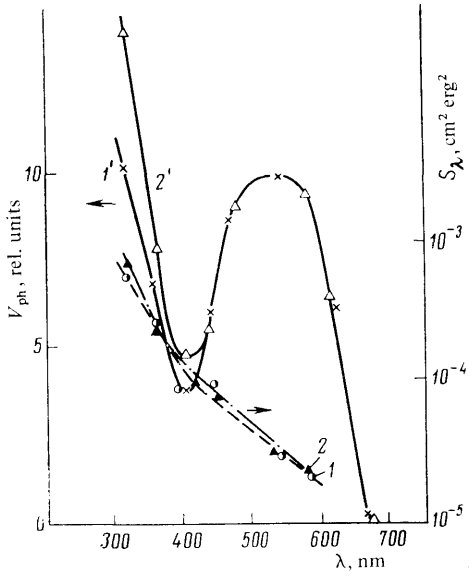


Figure 17. *EP*-sensitivity (curves *1* and *2*) and photo-e.m.f. (curves *1'* and *2'*) spectra of polydiphenylbutadiyne layers obtained from solution (curves *1* and *1'*) and by evaporation in a high vacuum (curves *2* and *2'*).[44]

A characteristic feature of polyphenylacetylene layers obtained by vacuum sputtering[44] is an increase of the mobility of charge carriers from 7×10^{-5} cm^2 V^{-1} s^{-1}, a value characteristic of layers obtained by casting from solution, to 0.07–0.01 cm^2 V^{-1} s^{-1}.[45,78] The energy required to generate a single electron–hole pair has been shown[45] to depend on the nature of the polymer, its structure, and the evaporation conditions; it can reach high values (300–500 eV), which indicates a complex mechanism of the generation of charge carriers.

A comparative study of the photo-e.m.f. and EP-sensitivity spectra for two types of layers (obtained from solution and by vacuum evaporation) (Fig. 17) showed that they are virtually the same and that there are therefore no differences between the quantum efficiencies of the generation in such layers. An important advantage of the layers obtained by vacuum sputtering is high optical quality, comparable to the quality of inorganic vitreous photoconductor films such as those of selenium.

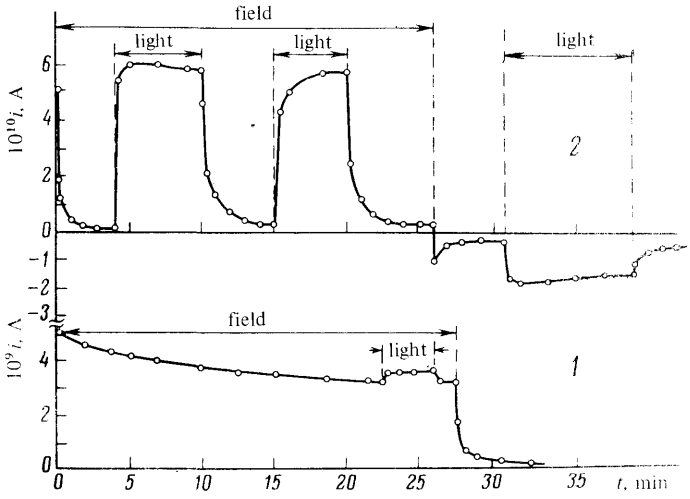


Figure 18. Kinetics of the photoconduction in PDPB layers obtained from solution (1) and by evaporation in a high vacuum (2).[44]

In conclusion we shall note yet another difference between the properties of the layers—the difference between the kinetic characteristics of the photoconductivity and polarisation phenomena (Fig. 18). The non-monotonic establishment of a stationary photocurrent (transverse photoconductivity conditions) in the course of the first illumination and the presence of depolarisation currents are characteristic of high-resistance compounds, both inorganic[79] and organic[80,81], although they have not been observed for a whole series of substances, particularly for many organic dyes[82]. In the PDPB layers of the two types under consideration these phenomena are manifested fairly clearly, which can be seen from the kinetic curves in Fig. 18.[44] When an electric field is applied, the dark polarisation-type current decreases more slowly for the layers obtained from solution. The dark current in these layers is higher by an order of magnitude than in the layers obtained by vacuum sputtering, which is correlated with the reduced "memory" under the EP conditions. Next, when the first light II-pulse is applied to a layer in an electric field, the photocurrent reaches a stationary value after passing through a maximum, although in subsequent exposures a stationary current is established monotonically (curve *2*). A monotonic form of the curve is also observed for PDPB layers of the other type (curve *1*). When the field is removed from the specimen (curve *2*), a depolarisation current is observed and in the subsequent

exposure there is a depolarisation photocurrent. For the other type of layers, depolarisation effects were not observed.

We may note that both types of layers exhibit hole conductivity, which has been established on the basis of the sign of the photo-e.m.f. and the nature of the photodischarge curves under EP conditions. The relaxation characteristics described[44] were obtained for the transverse conductivity of the layers in a field of 10^4 V cm^{-1}. Under EP conditions (longitudinal photoconductivity) in fields of 2×10^5 V cm^{-1}, such slow kinetic effects are not manifested, although a tendency towards polarisation effects can be responsible for the decrease of the EP sensitivity with decrease of field strength.

3. POLYMERS WITH CONJUGATED CARBON–NITROGEN BONDS

Polymers of this class exhibit an electrical conductivity of $10^{-10} - 10^{-13}\ \Omega^{-1}$ cm^{-1}. Their EP properties vary within wide limits depending on the molecular and supermolecular structures[50]. Under these conditions, the light relaxation curves for layers based both on the monomers and on the polymers have two sections—with rapid and slow rates of relaxation and a fairly high residual potential.

Layers based on monomers (benzylideneaniline, 2,3-diphenylquinoxaline, and dibenzylidene-*p*-phenylenediamine) have low limiting electric field strengths and do not exhibit an appreciable photoeffect. The introduction of the benzidine group into benzylideneaniline or *meta*-substituted benzene rings leads to an appreciable increase of the limiting field strength (up to 20 V m^{-1}). At the same time EP sensitivity appears in the ultraviolet. The maximum quantum efficiency is 1.5×10^{-5} quantum^{-1}.

Layers based on poly-Schiff bases have a limiting field strength which varies within wide limits (10–200 V μm^{-1}). Almost all the polymers sensitised exhibit EP sensitivity in the ultraviolet. Its magnitude increases, as for the monomers, when a benzidine group or *meta*-substituted benzene rings are introduced into benzylideneaniline. Polymers obtained from *p*-phenylenediamine and benzil with an excess of the diamine exhibits the highest limit sensitivity (quantum efficiency 1×10^{-4} quantum^{-1}), whereas the quantum efficiency of polymers obtained with an excess of benzil is lower (4×10^{-5} quantum^{-1}). The EP sensitivity is almost independent of the length of the molecular chain but depends strongly on the regularity of the supermolecular structure: for many polymers in the crystalline state, it is higher by an order of magnitude than in the amorphous state. It is noteworthy that hydrogenation also leads to the appearance of light sensitivity in amorphous polymers and block copolymerisation both increases and decreases the light sensitivity of the initial polymers.

We may note a characteristic feature of the above monomeric and polymeric layers, which consists of the "memory" of the previous history of the layer. In contrast to the familiar instances of "memory" in organic photoconductors, characterised by a monotonic variation of the light sensitivity, for polymeric photoconductors of the above class the memory involves relations with an extremum, for example, in the limiting potential and in the EP sensitivity of the "memory" layers and in the number of charging-exposure cycles. The light sensitivity of such layers passes through a maximum[50].

The observed characteristics of the influence of the molecular and supermolecular structures on the photoconductivity can be interpretated within the framework of the following general ideas. The photocurrent depends on the conditions governing the generation, transport, and recombination of charge carriers and all three stages can depend on the molecular and supermolecular structures. In particular, an enhancement of the delocalisation of electrons along the conjugation chain of the molecule and an increase of the regularity of the supermolecular structure should, by improving the transport conditions, lead to an increase of light sensitivity. As shown above, light sensitivity does indeed increase with increasing regularity of the structure (on transition from the amorphous to the crystalline state).

The nature of the possible influence of the molecular structure is more complex. The experimentally observed increase of the quantum efficiency of polymers when the delocalisation of electrons along the conjugation chain is weakened (primarily by the introduction of the benzidine group and *meta*-substituted benzene rings) is apparently associated with the increase of the efficiency of the generation of electron–hole pairs, which proceeds via an exciton stage. The impairment of the conditions for the transport of free carriers in this instance is probably not of decisive importance for the EP sensitivity in consequence of the presence of a strong electric field, which is responsible for the appreciable migration of the carriers even when their mobility is low. However, the regularity of the structure in the case of exciton generation can alter significantly the diffusion distance of the excitons, reducing the probability of their decomposition (accompanied by the generation of free carriers) and thereby influencing actively not only the transport stage but also the stage in which charge carriers are photogenerated.

IV. SPECTRAL SENSITISATION OF THE ELECTROPHOTOGRAPHIC RESPONSE

The spectral sensitisation of polymers is of considerable interest not only from practical but also from theoretical points of view[55,83-87]. The current hypotheses concerning the mechanism of spectral sensitisation are based on two alternative process mechanisms[88-90]: involving the transfer of excitation energy from the dye molecule to the photoconductor, under the influence of which a free charge carrier subsequently appears, or the transfer of a photoelectron to the excited dye molecule. There is at present no unambiguous experimental evidence in support of one or other mechanism, but, presumably, if the excitation energy transfer mechanism operates in a substance with exciton generation of photocarriers, then the spectral sensitisation can be regarded as the "pumping" of the energy absorbed by the dye into the sensitised photoconductor; the quantum yield η in the sensitisation region is then determined by the value of η of the sensitised photoconductor. Organic polymeric photoconductors with exciton generation of photocarriers then exist under very unfavourable conditions, since their quantum yield of the internal photoeffect in the visible region is low, which is due to fundamental causes arising from the exciton generation mechanism[60]. The conditions governing the dissociation of excitons can be made easier and the quantum yield increased by the formation of charge-transfer complexes from the initial polymers.

In the study of sensitisation, two extreme cases, differing in the concentration of dye molecules in relation to the sensitised polymer or the CTC based on it, are of interest. The first case involves high concentrations of carriers. The greatest number of studies have been devoted to it and extensive data have now been obtained for the quantum yields in the generation of photoholes from complexes based on polyvinylcarbazole (PVCA) on sensitisation with triarylmethane and pyrylium dyes, monomethinecyanines, and trimethinecyanines.[1,91] The quantum yield in the region of sensitisation reaches 50%. However, the use of high concentrations of dyes and CTC makes the system heterophase; an opalescence usually appears and the resolution diminishes. Such a system does not exhibit thermomechanical properties important for applications in a photothermoplastic EP process.

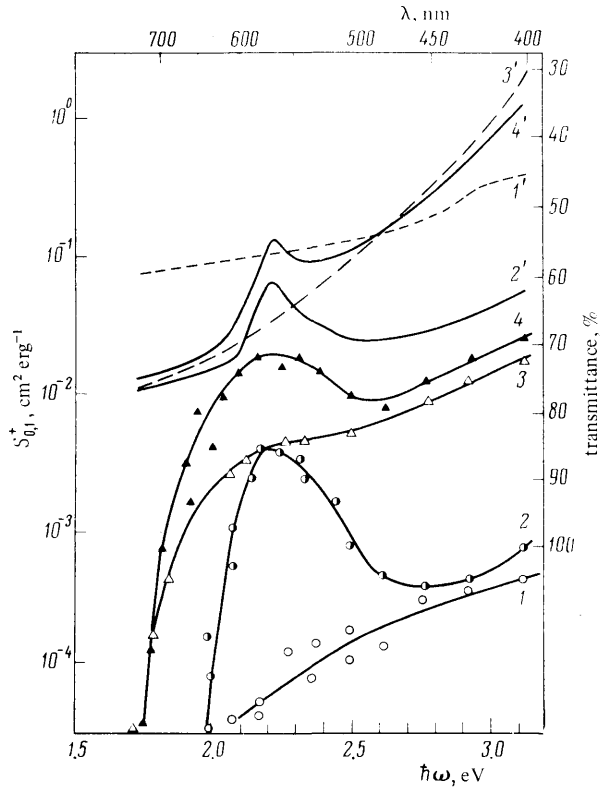


Figure 19. EP-sensitivity spectra of PVCA (curve *1*) and PVCA–TNF charge-transfer complex (curve *3*) layers; 2) and 4) corresponding layers sensitised by rhodamine B; 1′)–4′) transmission spectra of layers *1–4* respectively[92] ($S_{0,1}$—spectral sensitivity in absolute energy units).

The above disadvantages can be eliminated by reducing the concentrations of CTC and dyes (second case), but the nature of the phenomenon can then be significantly altered. As in the first case the formation of complexes and the sensitisation of PVCA by dyes causes a significant increase of the EP sensitivity of PVCA [92] (Fig.19). In order to examine the nature of the effect, we turn to Fig.20, which illustrates the absorption spectra and the spectral sensitivity of optically homogeneous layers of PVCA and its complexes as well as layers sensitised by rhodamine B.[93] Fig. 20 shows that the charge-transfer complex exhibits a broader absorption region than the initial polymer and a much higher light sensitivity (curve *3*). One need only note that the efficiency in relation to the absorbed energy at the maximum does not exceed 20% (taking into account the reflection). The sensitisation by rhodamine B increases by a factor of ~15 the light sensitivity of the polymer and by a factor of 5 that of its charge-transfer complex. The absolute quantum yields of the internal photoeffect at the 567 nm absorption maximum (in the presence of a superimposed electric field of 7×10^{-5} V cm^{-1}) are as follows:

Layer	PVCA	CTC	PVCA sensitisation by rhodamine B	CTC sensitisation by rhodamine B
η, %	~1	3.3	1.1	3.6

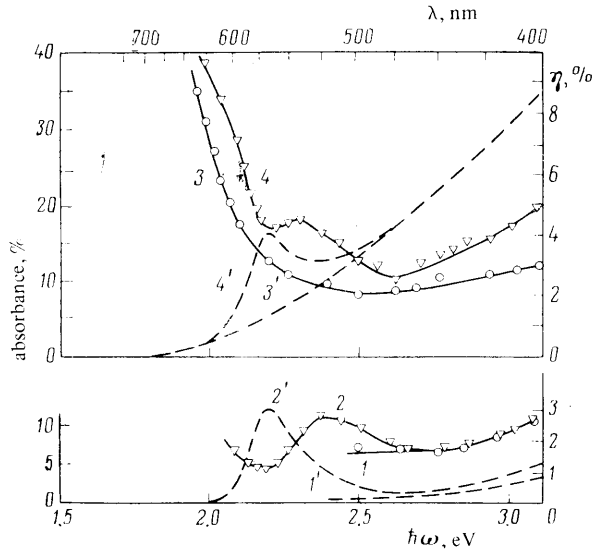


Figure 20. Quantum yield spectra (η is the absolute quantum yield of charge carriers per quantum, %) of the internal photoeffect (curves *1–4*) and the absorption spectra (curves *1′–4′*) of PVCA (curves *1* and *1′*), PVCA sensitised by rhodamine (curves *2* and *2′*), PVCA–TNF charge-transfer complex (curves *3* and *3′*), and PVCA–TNF charge-transfer complex sensitised by rhodamine B (curves *4* and *4′*) [93]; dye concentration 0.28 mole %; trinitrofluorenone concentration 3.2 mole %.

Thus the efficiency of the sensitisation, defined as the ratio of η at the sensitisation maximum to η for the initial polymer, remains constant and close to 100% despite the different initial values of η. The relation obtained shows that the mechanism of the spectral sensitisation in the case of exciton generation under consideration is due to the "pumping" of energy into the polymer by the dye. In both instances of sensitisation examined, its efficiency must therefore be regarded as a maximum and the light sensitivity is limited solely by the fraction of energy absorbed in the layer.

We may note that, as can be clearly seen from the experimental data (Fig. 20, curves *3* and *4*), the introduction of a dye leads to an increase of the quantum yield not only in the region of the sensitisation of the CTC but also in the region of shorter wavelengths, which may be evidence for the formation of complexes in the PVCA–dye systems. In this sense, the sensitisation of PVCA by dyes leads to the possibility of increasing the quantum yield over a much wider region of the spectrum in the short-wavelength range compared with the absorption spectrum of the sensitiser dye.

V. INJECTION SENSITISATION OF THE ELECTROPHOTOGRAPHIC RESPONSE

The increase of light sensitivity and the extension of the region in which it occurs for polymeric photoconductors can be achieved by injection sensitisation based on the phenomenon of photoinjection in film heterostructures. The principle of the construction of heterostructures with EP sensitivity makes it possible to control the properties of the layers, in the sense of extending the width of the region of spectral sensitivity and improving the memory, and ensures the thermoplastic visualisation of the latent image in the presence of the appropriate thermomechanical properties of the component which does not carry the photogeneration function[94]. Among all the possibilities enumerated above, the case of high light sensitivity achieved by the photoinjection of carriers, which ensures their transfer through the heterostructure, is of greatest interest.

A heterostructure with EP sensitivity is nowadays achieved on the basis of inorganic systems, because an organic component as a rule gives rise to a potential carrier, which prevents injection[95]. A system containing selenium and PVCA is exceptional in this respect[96,97], but here injection has been observed only from heterophase *p*-selenium, which did not ensure a high resolution.

High-resolution heterostructures based on amorphous forms of selenium and thermoplastic compositions based on PVCA have been investigated recently[94]. The heterostructures were made in glass frames with a conducting layer of lead dioxide on which layers of *n*- and *p*-type selenium and PVCA 0.1–0.3 μm thick were deposited in succession. The study of dark EP properties of the above heterostructures showed that, for the negative surface charge corresponding to the injection of holes into PVCA, the associated limiting field strength (3×10^5 V cm^{-1}) corresponds to that observed for selenium layers and the dark relaxation time corresponds to that for PVCA layers. The retention of properties indicated above (in contrast to, for example, selenium–polystyrene heterostructures[95]) indicates the absence of an energy barrier at the inner boundary of the heterostructures when a field (of definite polarity) is imposed. The absence of a barrier is important for ensuring the possibility of the transfer of carriers, generated in selenium, through the heterostructure and, according to preliminary EPR data, can be associated with the formation of a charge-transfer complex at the selenium–PVCA boundary. In fact, on the one hand, the ability of polycyclic aromatic systems, including PVCA, to form charge-transfer complexes with electron acceptors is known and, on the other hand, the ability to add an additional electron to the electron shell is characteristic of atoms with an unfilled outer electron shell (the *p*-shell in selenium is unfilled).

The shape of the photodischarge curves confirms the photoinjection of holes and the absence of the injection of electrons. Injection is observed from both *p*- and *n*-type selenium, which is due to the mixed nature of the photoconductivity of the two forms of selenium. At any rate, an electron-hole pair is initially photogenerated in selenium after which carriers predominating in PVCA (holes) are injected through the boundary and transported through PVCA.

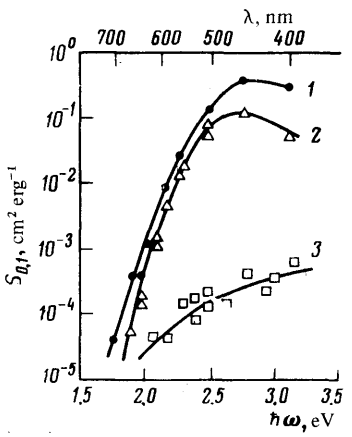


Figure 21. EP-sensitivity spectra of PVCA layers (2 μm thick) in injection sensitisation by selenium [94]: 1) *p*-Se (0.2 μm); 2) *n*-Se (0.3 μm); 3) no selenium.

The light sensitivity of the heterostructure significantly exceeds that of PVCA and in the region of strong absorption virtually corresponds to the light sensitivity of selenium layers, decreasing with increase of the wavelength owing to the decrease of the absorption of energy (Fig. 21), while the quantum yield η corresponds to η for amorphous forms of selenium over the entire spectral range investigated. The data in Fig. 21 were obtained for a field strength of 3×10^5 V cm^{-1}. The light sensitivity depends markedly on the field over the entire range of the spectrum and, in contrast to PVCA, there is a critical field of $\sim 6 \times 10^4$ V cm^{-1} for the heterostructure, below which there is no light sensitivity. If it is assumed that the traps in PVCA are small and that a space charge does not therefore arise on photodischarge, the threshold field can be interpreted as the field necessary to ensure the photoinjection of charge carriers from selenium into PVCA. The dependence of the light sensitivity of *n*-type selenium on the field can be naturally accounted for by the dependence of η on the field[60], or, in the case of *p*-type selenium, it is probably associated with the dependence of the conditions for the transport of carriers on the field.

Thus photoinjection in the heterostructures examined makes it possible to combine the high light sensitivity of selenium with the effective thermomechanical properties of compositions based on PVCA, which ensures the resolution of an element whose size does not exceed the wavelength of visible light when the light sensitivity is high.

VI. THE QUANTUM YIELD AND THE STRUCTURE OF POLYMERS

Systematic studies have demonstrated a fundamental difference between the spectra of the quantum yield of the internal photoeffect in polymeric photoconductors and classical semiconductor crystals such as those of germanium and silicon. Whereas the quantum yield in the above semiconductor crystals (which represents the number of free charge carriers generated by a single absorbed quantum) is constant over a considerable range of energies of the quantum and close to 100% up to the absorption limit, in polymeric photoconductors it is close to zero in the region of the absorption limit, increasing in the interior of the absorption band[60]. The photogeneration of charge carriers over a wide range of energies of the quanta via the state involving a Coulombically bound electron–hole pair (exciton) plays a decisive role in the establishment of the structure of the quantum yield spectrum. The probability of the separation of the pair depends on the kinetic energy of the electron which has absorbed the quantum and on the rate of loss of this energy. The reverse recombination of the electron with its "own" hole or its "own" ion, which leads to a non-photoactive absorption, takes place as a result of the decrease of the kinetic energy of the electron to the thermal energy level before the electron moves outside the limits of the sphere of the Coulombic field of its partner in which the electron attraction energy exceeds the $\frac{3}{2}kT$ level. The external electric field facilitates the photogeneration process by reducing the Coulombic barrier and increasing thereby the probability of the escape of the carrier (the Frenkel–Poole effect).

We shall now consider the spectra of the quantum yield of the internal photoeffect in anthracene single crystals, polyconjugated polymers of the same electronic type as anthracene (polymers of the acetylene series), and saturated polymers having the same composition as anthracene (polystyrene and other polymers of the vinyl series).

Unique possibilities for the investigation of the absolute quantum yield of the internal photoeffect arise under EP conditions. To achieve such conditions, an ionic contact is made with the surface of the layer located on a conducting support. The density of the ionic charge, generated by the ionisation of air molecules, reaches 10^{12} cm^{-2} for an average interionic distance of 100 Å. Such contact ensures optical transparency over the entire experimental part of the spectrum and the maximum possible electric field strength which is not limited by the "weak sites" in the layer in view of the absence of longitudinal conductivity and which makes it possible to obtain saturation currents for substances with a low mobility of charge carriers such as the photoconductors investigated. Furthermore, the ionic contact ensures a virtually complete exclusion of an external photoeffect in the ultraviolet, which is limited to the strong fields of the electrical double layer formed, reaching 10^6 V cm^{-1}.

The number of charge carriers n generated by light is related to the change in the potential of the layer ΔV when the carriers have been completely collected, by the expression

$$n = \varepsilon \cdot \Delta V/4\pi de|_{\Delta V \to 0},$$

where ϵ is the dielectric constant and D the effective thickness of the layer. The condition $\Delta V \to 0$ ensures a quasi-stationary potential. One of the fundamental difficulties when the EP method is used involves demonstrating the complete collection of carriers; several pieces of evidence in support of this claim can be adduced:

(1) the presence of a linear section on the photodischarge curve.

(2) Direct calculation of the shift of charge carriers. Thus a 100% collection coefficient for electrons and holes was ensured in single-crystal anthracene layers 15 to 20 μm thick[51]. The mobility of holes $\mu_g = 5 \times 10^{-1}$ cm^2 m^{-1} s^{-1}, $E = (2-20) \times 10^4$ V cm^{-1}, and $d = 20$ μm; the time of flight of holes $t_{fl} = d/\mu E = (2-20) \times 10^{-8}$ s is much shorter than $\tau_g = 3 \times 10^{-5}$ s (τ_g is the lifetime of holes); the electron mobility $\mu_e = 3 \times 10^{-1}$ cm^2 V^{-1} s^{-1} and the time of flight of electrons $t_{fl} = (3-30) \times 10^{-8}$ s^{-1} $\tau_e = 2 \times 10^{-6}$ s.

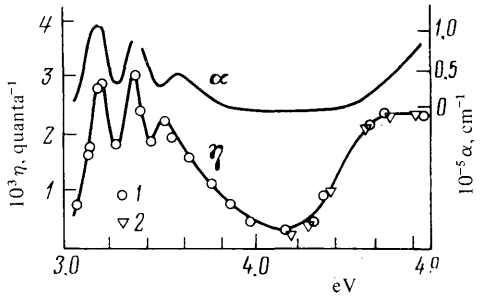


Figure 22. Absorption (α) and quantum yield (η) spectra of a single-crystal layer of anthracene[51,61]: 1) holes; 2) electrons; $E = 2 \times 10^5$ V cm^{-1}.

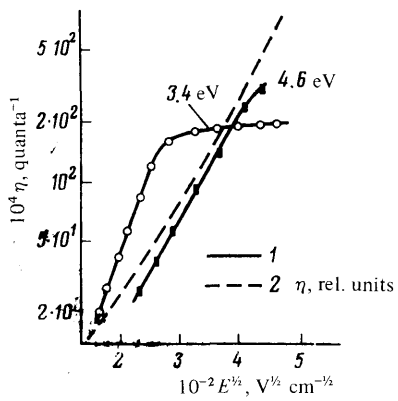


Figure 23. Dependence of the quantum yield for anthracene layers on the electric field[60]: 1) experimental data; 2) calculated data.

For polystyrene (PS) layers, we have $\mu_g = 10^{-4}$ cm^2 V^{-1} s^{-1}, $E = (4-15) \times 10^5$ V cm^{-1}, $d = 0.3$ μm, and $t_{fl} = (2-8) \times 10^{-7}$ s $< \tau_g = 1 \times 10^{-6}$ s (estimate under EP conditions from $\mu\tau$ for $\eta = 100\%$). For polyacetylene layers, particularly for polydiphenylacetylene, $\mu = 5 \times 10^{-4}$–6.5×10^{-5} cm^2 V^{-1} s^{-1}, which also ensures a complete collection of carriers.

(3) Whereas it is known that in the region of strong absorption 100% collection of carriers is ensured, in the region of weak absorption, which softens the collection conditions, the collection can also be complete. A decrease of light sensitivity with decrease of absorption coefficient is in this case caused solely by a change in generation conditions.

An exceptional value of η close to 100% can also serve as evidence for complete collection.

In order to eliminate the influence of space charge in the measurement of $\eta(E)$, a family of photodischarge curves at different initial potentials was obtained. It is noteworthy that, when η depends on E, a linear photodischarge plot is not observed even in the region of complete collection ($\mu\tau E = d$) (the current is not saturated).

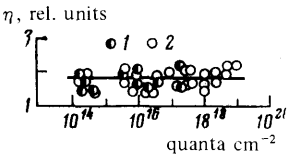


Figure 24. Dependence of the quantum yield for an anthracene layer on the ionisation density[95] ($E = 2 \times 10^5$ V cm^{-1}): 1) 3.4 eV; 2) 4.1 eV.

For anthracene, the spectrum of η values in the region of energies of the quanta $\hbar\omega$ less than the width of the forbidden gap $E_g = 3.9$ eV is associated with the diffusion of molecular excitons (with a small radius) to the surface and corresponds to the optical absorption spectrum (Fig.22). In the region where $\hbar\omega > E_g$, η increases with increase in $\hbar\omega$. In both regions the photogeneration is controlled by the electric field (Fig. 23). The influence of the field cannot be associated with the change in the conditions for the recombination of free carriers, since there is no dependence of the quantum yield on the ionisation density within the limits of five orders of magnitude (Fig. 24) and the change in the saturation of generation centres as the field strength is varied in the region of $\hbar\omega < E_d$ would lead to a decrease of η with increase of the field.

The effect of the field in the region of molecular excitons indicates the existence of an intermediate state in the formation of free carriers as a result of the interaction of the exciton with a centre (in anthracene this can be oxygen) having a high electron affinity and weakening the electron–hole interaction of the Coulombically bound electron-hole pair. The probability of the escape of one of the carriers of the pair from the stationary (in the interaction with the centre) or mobile partner is determined by the electric field (Fig. 23). There is a threshold quantum energy $\hbar\omega \simeq E_g$, above which there is a finite probability that the primary pair gives rise to free carriers as a result of an excess energy equal to $\hbar\omega - E_g$. In this region η is therefore independent of the absorption coefficient α and increases with increase of $\hbar\omega$. In the region where $\hbar\omega < E_g$ it is necessary to supply an additional energy to the pair in order to cover the energy deficiency; in the given instance this energy is drawn from the crystal lattice (the generation centres). For the operation of this mechanism, the bound pair (exciton) must be mobile if the generation centres are mainly in the surface region. The difference between the dependences of η on the field in the two regions, namely the occurrence of saturation and a different slope of the $\eta(E)$ relation when the Frenkel–Poole law $\lg\eta \propto E^{1/2}$ holds over a wide range of E values in the given model, can be explained by the limited number of generation centres, so that all the excitons interacting with the centres in fields of 2×10^5 V cm^{-1} give rise to free carriers. The change in the slope of the $\eta(E)$ line is due to the change of the constant in the Frenkel–Poole equation: in the region where $\hbar\omega < E_g$ charge carriers escape from the stationary centre (in this region only holes are mobile), while in the region where $\hbar\omega > E_g$ the carriers move away from one another ($\eta_e \simeq \eta_h$).

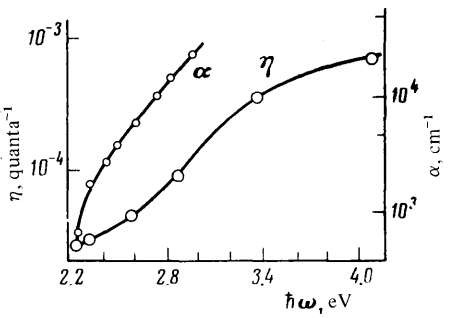


Figure 25. Absorption (α) and quantum yield (η) spectra for PDPB layers[95].

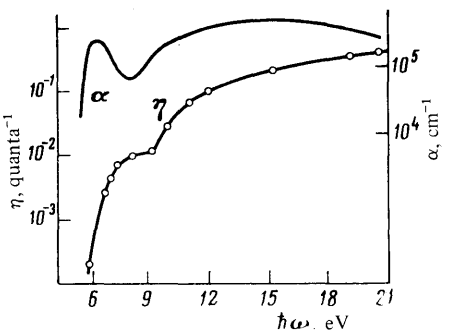


Figure 26. Absorption (α) and quantum yield (η) spectra for a polystyrene layer[15].

Polyacetylenes (Fig. 25—polydiphenylbutadiyne) and polymers of the vinyl series (Fig. 26—polystyrene) in the amorphous state are also characterised by a value of η which increases with increase of $\hbar\omega$ and E. The maximum value of η for PDPB is of the same order of magnitude as the value for molecular crystals (this question is discussed in greater detail elsewhere by one of the authors of the review[60]).

The relations obtained indicate the occurrence of exciton effects in molecular, crystalline, and amorphous photoconductors, which lead to a broad region of non-photoactive absorption at the edge of the spectrum. The probability of the decomposition of the primary bound states arising following the absorption of a light quantum depends on the structure of the photoconductor, which leads to the possibility of the structural sensitisation of the photoeffect.

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Excess Electrons in Non-polar Molecular Liquids

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The results of recent experimental and theoretical studies of the properties of an excess electron in non-polar liquids have been summarised. Various models of electron transfer, and the role of localised and quasi-free states of the excess electron in chemical reactions have been discussed. The bibliography contains 142 references.

CONTENTS

I. Introduction 615
II. The mobility and energy of an excess electron 616
III. Chemical reactions 621

I. INTRODUCTION

The discovery of the solvated electron in water about fifteen years ago laid the foundation for intensive studies of the properties of a "chemically non-combined" or excess electron in molecular liquids. Until recently, these studies were related chiefly to polar media. It was found that an excess electron is one of the most chemically active species and plays an important role in many electrical, photochemical, and radiation-chemical processes[1-4].

Until 1968, experimental studies of the excess electron in non-polar liquids were restricted to the study of the mobility of the electron in liquefied noble gases and diatomic liquids (this work has been reviewed[5-7]). In the last few years, the study of the properties and elementary chemical reactions of the excess electron has been extended to liquids consisting of complex non-polar molecules—liquid hydrocarbons and various organosilicon compounds. This has been made possible by the development of the technique of recording fast reactions, particularly the use of nanosecond techniques, and the improvement of methods of purifying liquids from electron acceptors.

Intensive studies in this field began after the possibility of recording an excess electron in liquid hydrocarbons had been demonstrated in the period 1968–1970[8-11].

A large amount of factual material relating to the study of the physical properties and reactivity of an excess electron in non-polar liquids has now accumulated. It has been found that the excess electron is a much more active species in these media than in the polar liquids. The direct experimental data obtained on the mobility and rate constants of the reaction of the electron differed so sharply from the values previously assumed that they led to a change in ideas regarding the time scale of processes involving an excess electron in photochemical and radiation-chemical changes in non-polar liquids. New data are extending the possibility of studying reactions with electron transfer in condensed media. These data can be used in the physics of dielectrics to study the initial stages of electric breakdown, and in experimental nuclear physics to create liquid ionisation chambers. This explains the increasing interest shown by specialists in different fields in the study of the properties of the excess electron in non-polar liquids.

The problems of the behaviour of an electron in molecular liquids, including non-polar liquids, have been reviewed[12-14]. The present review summarises the results of work published up to 1977. Particular attention has been paid to the mobility and reactivity of an excess electron in liquid hydrocarbons. In the last part of the review, new data on the properties of the excess electron are used to discuss the kinetics of the primary electronic processes of the radiolysis of non-polar molecular liquids.

II. THE MOBILITY AND ENERGY OF AN EXCESS ELECTRON

The experimental data at present available on the mobility and reactivity of the excess electron in non-polar liquids relate chiefly to an electron in thermal equilibrium with the medium. In polar liquids, the state of an equilibrium excess electron is localised. The electron in this state is in a potential well, formed as a result of the polarisation interaction of the electron with the dipolar molecules of the medium. For an excess electron in non-polar liquids, generally speaking, it is not clear whether the equilibrium state is localised, since the orientational polarisability of molecules in these media does not play a significant role in the localisation of an electron. According to existing views of the states of an electron in disordered systems[15,16], at thermal equilibrium in a non-polar liquid an excess electron can in principle also exist in a delocalised state. In this state the electron occupies the volume of many molecules, and its interaction with the medium is determined only by their electronic polarisability. It is assumed that the delocalised or quasi-free electron has a much higher mobility than an ion.

As shown below, data on the mobility of the excess electron indicate that in many non-polar liquids an equilibrium electron is neither completely localised nor quasi-free, but is most probably in neither state. It is still possible, however, to regard an excess electron as a species in an "equilibrium" state in processes for which the characteristic time is greater than the relaxation time of various states of the electron. Processes of this kind are usually dealt with in experimental studies of the mobility and rates of chemical reactions of an excess electron in non-polar liquids.

1. Measurements of Drift Mobility

The drift mobility μ or the ratio of the average velocity of the electron v in an electric field to the field strength E

$$\mu = v/E \qquad (1)$$

is one of the most definite characteristics of the motion of an electron in a liquid. Einstein's relationship makes it possible to relate μ to the coefficient of diffusion of the electron $D = k_B T/e\mu$, where k_B is the Boltzmann constant, T the absolute temperature, and e the charge of the electron.

The first reliable measurements of the value of μ for an excess electron in liquid hydrocarbons were made comparatively recently, in 1968–1969[9-11]. It has now become clear that the failure of the many earlier attempts to carry out these measurements were due to the use of liquids not sufficiently purified from electron acceptors. In most cases, rapid disappearance of the excess electrons and the formation of the negative ions of the acceptor molecules took place. A direct indication of the existence in liquid hydrocarbons of current carriers more mobile than ions was obtained by Tewari and Freeman[8], who detected the formation of short-lived charged species in liquid neopentane under the influence of ionising radiation. The use of thoroughly purified liquids in later work made it possible to determine the average velocity of these species in an electric field from the time of flight over the distance between two electrodes.

The values of μ obtained from these measurements were 10^2–10^5 times greater than the mobility of ions, so that the current carriers recorded were identified as excess electrons. This conclusion was confirmed by studies[10] of the current of electrons photo-injected from a metal into "pure" liquid hydrocarbons. These studies gave the same values of μ.

The purity of the liquids required for the measurement of the time of flight of excess electrons over the distance between electrodes (t_f) can be judged from the lifetime of electrons before their capture by the molecules of acceptors, which in these measurements must be greater than t_f. The acceptable concentration of electron acceptors, estimated from this condition and the known rate constants of reactions involving the capture of an excess electron, often did not exceed 10^{13} cm^{-3}.

The mobilities of excess electrons have now been measured for more than fifty different non-polar molecular liquids, including saturated[9-11,18-38], unsaturated[18,34,39], normal, cyclic[34], and aromatic[40] hydrocarbons, and various organosilicon compounds, such as tetramethylsilane[11,21]. Table 1 gives some published values of μ for liquids at room temperature. More complete data have been published[12-14,38]. The results lead to the following general conclusions.

Table 1. Drift mobility of an excess electron μ, activation energy of the mobility E and the energy of the ground level of a quasi-free electron V_0 in non-polar molecular liquids.

Liquid	T, K	μ, ($cm^2 V^{-1} s^{-1}$)	E, eV	V_0, eV
Tetramethylsilane	296	90[11]	0.018[11]	−0.61[42], −0.62[41] −0.55[43], −0.51[47]
Neopentane	296	70[26,40]	—	−0.43[41,42], −0.35[43]
2,2,4,4-Tetramethylpentane	295	24[21]	0.064[21]	−0.33[50]
2,2,5,5-Tetramethylhexane	293	12[21]	0.05[21]	—
2,2-Dimethylbutane	296	10.9[11]	0.052[11]	−0.24[42], −0.15[46]
2,2,4-Trimethylpentane	296	7[11]	0.06[17], 0.51[33], 0.046[36]	−0.15[42], −0.18[41] −0.14[43], −0.19[52]
Cyclopentane	296	1.1[11]	—	0.17[43], 0.28[42]
Cyclohexane	294	0.35[11], 0.45[21]	0.17[21]	0.01[50]
Butane	296	0.4[11]	—	—
n-Pentane	293	0.15[74]	—	0.01[47]
Benzene	293	0.114[40]	0.32[40]	−0.14[44]
n-Hexane	296	0.09[11], 0.082[29]	0.19[18,28,33] 0.16[36]	−0.09[42], 0.04[41] 0.16[49], 0.2[47]
Toluene	292	0.063[40]	0.15[40]	−0.22[44]
n-Decane	296	0.038[36]	0.21[36]	0.18[49]
n-Pentadecane	296	0.03[35]	0.16[35]	—
Methane	111	400[22,25]	—	0.0[48]
	140	430[20]	−0.007[30]	—
Ethane	130	0.014[30]	0.08[30]	0.22[46]
Propane	175	0.05[30]	—	0.11[50]

1. The mobility of an electron in different liquids, even at a given temperature, cover a wide range of values: from 3×10^{-2} cm^{2}V^{-1}s^{-1} in n-decane to 10^2 cm^{2}V^{-1}s^{-1} in neopentane and tetramethylsilane. The mobility of the

electron is unusually "sensitive" to the structure of the molecules of the liquid. For example, for n-pentane and neopentane the values of μ differ by a factor of more than 400. The mobilities of the electron in *cis*- and *trans*-butenes differ by a factor of approximately 100. For normal hydrocarbons, the mobility at first decreases rapidly with increase in the number of carbon atoms from two to six. Further increase in the number of carbon atoms leads to only a slight change in μ. The position of the double bond in a molecule determines whether μ increases or decreases. It is difficult to relate the influence of the structure of molecules on the mobility of an excess electron to any single property of the molecules of the liquid. The nature of the movement of an electron in liquid saturated hydrocarbons apparently depends to a considerable extent on the shape of the molecule: more spherically symmetrical molecules correspond to a greater mobility. The greatest mobilities are shown by electrons in methane, neopentane, and tetramethylsilane, which have highly symmetrical molecules.

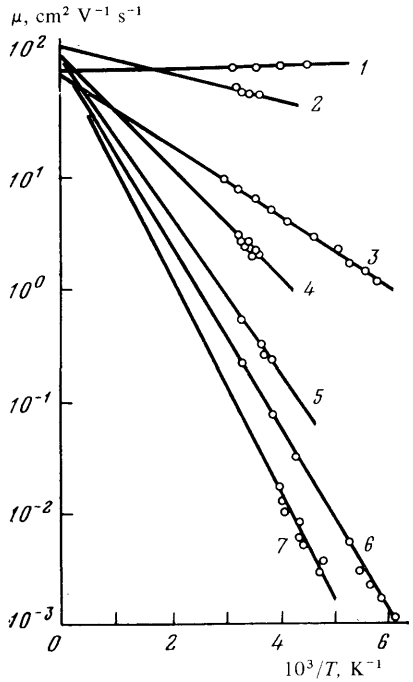


Figure 1. Temperature dependence of the drift potential of an excess electron in various molecular liquids: 1) tetramethylsilane[33], 2) neopentane[20], 3) iso-octane[17], 4) 2-methylbut-2-ene[20], 5) 66% n-hexane in neopentane[20], 6) 3-methylpentane[66], 7) n-hexane[20].

2. For all hydrocarbons studied, except liquid methane[35], the mobility of the electron decreases with decrease in temperature (Fig. 1). The temperature dependence of μ for most saturated hydrocarbons is described by the Arrhenius equation

$$\mu = \mu_0' \exp(-E/k_B T) \qquad (2)$$

with pre-exponential factors μ_0' from 10^2 $cm^2V^{-1}s^{-1}$ to 10^3 $cm^2V^{-1}s^{-1}$. The $\mu(T)$ relationship for liquid ethane and n-pentane is more complex. The activation energy increases with decrease in T in the first case, and decreases in the second. $\mu(T)$ relationships of this kind are also typical of unsaturated hydrocarbons.

3. The mobility of the excess electron is independent of the electric field strength, that is $v \sim E$ up to values of $E \simeq 10^4$ V cm^{-1}. In liquids with a relatively high mobility (liquefied methanol, neopentane, iso-octane), further increase in E leads to a decrease in μ.[23,26,32] In this range of values of E, the velocity of the electron $v \sim E^{0.5}$. This $v(E)$ relationship is characteristic of the movement of an electron in semiconductors, and is usually related to an increase in the average kinetic energy of the electron in the electric field. Another type of relationship was established for liquids with a low mobility: in the range of strong fields, μ increases with increase in E (liquefied ethane, propane, pentane[25-27,38]). A similar relationship was previously found for substances in which the movement of the electron takes place in hops from one localised state to another. It is assumed that in this so-called "hopping" mechanism of electron transfer, the electric field increases the probability of a hop.

4. The mobility of an electron shows a correlation with the energy V_0 of the ground state of the quasi-free electron in the liquid, that is with the energy which must be expended to transfer a stationary electron from a vacuum to a lower delocalised state in the liquid. As a rule, the lower V_0, the higher the mobility of the excess electron. This dependence of μ on V_0 is one of the characteristic features of the movement of an electron in non-polar liquids (for polar liquids, a correlation between μ and V_0 has not been established). It is assumed that the position of the level of a quasi-free electron in some cases also determines the reactivity of the excess electron (see Part III). It is therefore not surprising that the discussion of data on V_0 at present occupies an important place in the examination of the properties of an excess electron in non-polar liquids.

2. Energy of a Quasi-Free Electron

Data on the magnitude of V_0 for non-polar liquids have been obtained chiefly by two methods: from the difference in the work functions for an electron from a metal in a vacuum φ_V and in a liquid φ_l,[41-49] or from the difference in the ionisation potentials of the molecules in the gas I_g and in the liquid I_l.[50,51] The energy of the quasi-free electron is determined in the first method as the difference $V_0 = I_l - \varphi_V$, and in the second case as $V_0 = I_l - I_g - P_+$, where P_+ is the energy of the polarisation of the positive ion in the liquid. The results obtained by the two methods show good agreement.

The values obtained for V_0 for non-polar liquids (see Table 1) lie in a range from −0.6 eV to +0.2 eV, that is they are much higher than the corresponding values for polar liquids (for example, for water $V_0 = -1.3$ eV[4]). Positive values of V_0 mean that it is energetically more favourable for the electron to move into a vacuum from the quasi-free state in the liquid. Experimental confirmation of the existence of this transition is provided by the observation of the effective emission of excess electrons from liquid n-hexane and iso-octane into the gaseous phase[52,53].

A number of attempts have been made to interpret the properties of a quasi-free electron in non-polar molecular liquids using the same approach as in the case of liquefied

gases, since high values of V_0 were previously obtained for the latter. For liquefied gases, from data on the scattering of an electron by atoms in the gaseous phase, it is assumed that an electron cannot approach an atom to a distance less than the so-called radius of a "hard sphere" a. According to the theory[6], in this approach,

$$V_0 = T_k(a, n) + U(\alpha, n), \quad (3)$$

where T_k is the energy, often called "kinetic", although it is the energy of an electron at the foot of the conductivity zone. Physically, this energy is related to the same quantum effect as the increase in the energy of the ground state of an electron in a potential well when the walls of the well approach one another. The role of the walls in the model of the electron being considered is played by the surface of the "hard spheres". As expected from this interpretation, the value of T_k increases with increase in a or the number of molecules in unit volume n. The average polarisation energy U can be calculated[6] from the known polarisability of the atom α and the density of the liquid.

There are at present few data on the reaction of low-energy electrons with complex molecules in a liquid, so that there is much less justification for using this method of calculation for liquid hydrocarbons than in the case of atomic liquids. Nevertheless, the values calculated using Eqn. (3) show good agreement with experimental data in this case also (Fig. 2). The values of a used in this calculation show a qualitative correspondence to data on the scattering of electrons by hydrocarbon molecules in the gaseous phase[54]. Moreover, the calculation of V_0 for a mixture of hydrocarbons from the values of α and a for the components gives good agreement with experiment [14,55].

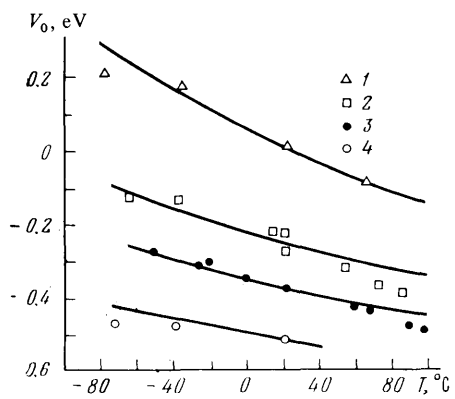


Figure 2. Temperature dependence of the energy of the ground state of a quasi-free electron in liquids. The points give the experimental data[47], and the continuous lines the results of a calculation[47] by the Wigner–Seitz method: 1) n-hexane, 2) iso-octane, 3) 2,2,4,4-tetramethylpentane, 4) tetramethylsilane.

3. Optical Absorption

Because of the high reactivity of an excess electron in non-polar liquids, the measurement of its optical absorption in these media, particularly at room temperature, is more complicated than that for polar liquids. At present, the optical absorption of an excess electron is known for only a few hydrocarbons: for propane at 88 K and 108 K,[56] 3-methylhexane at 193 K,[57] and methylcyclohexane at 160 K and 293 K.[58] In all cases the form of the absorption spectrum was found to be close to the spectrum of a trapped electron in solid amorphous hydrocarbons. Fig. 3 gives as an example the optical absorption spectra of an excess electron in liquid propane and solid 3-methylpentane.

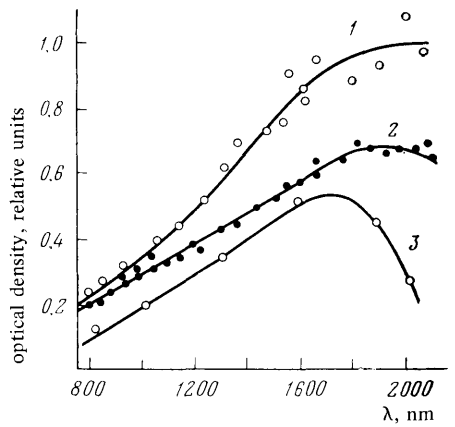


Figure 3. Spectral dependence of the optical absorption: 1) excess electron in liquid propane at 88 K[56] 2×10^{-6} s from the start of a generating pulse of duration 1×10^{-6} s; 2, 3) captured electron in solid amorphous 3-methylpentane at 77 K, 10^{-5} s (2) and 380 s (3) from the start of a generating pulse of duration 10^{-6} s.[59]

The observation of the optical absorption of an excess electron indicates that at least some of the electrons are in a localised state for times greater than the absorption recording time ($> 10^{-8}$ s). At present there is no generally accepted viewpoint on the nature of the localised state of an electron in liquid hydrocarbons. According to a general approach[60], localised states in a liquid may be formed as a result of the capture of an electron by several fluctuations, for example fluctuations in the density or the orientation of the molecules. Studies of the mobility of an electron in a mixture of hydrocarbons[23,29,31] also lead to the conclusion that several molecules take part in the formation of a localised electron.

Of the proposed mechanisms of the localisation of an excess electron in liquid hydrocarbons, the capture of the electron by a cavity between molecules has been examined in most detail[44,61,62]. A similar mechanism was established for liquid helium and neon[6,7], and is assumed for liquid hydrogen and nitrogen[63,64]. Studies of positron annihilation in a number of liquid hydrocarbons[65] confirmed the existence in these liquids of cavities having a radius of ~ 4 Å, suitable for electron capture. Cavities of this size are also postulated in the interpretation of the form of the optical absorption spectrum of a captured electron in solid amorphous hydrocarbons[66]. Numerical calculation[62] of a simple model of a cavity with rectangular walls (see Fig. 4) shows that an electron in a ~ 4 Å cavity may in fact be a stable system in liquid hydrocarbons. For this it must be assumed that the value of the dielectric constant close to the walls of the cavity, determining the energy of

the polarisation of the medium by a localised electron U_{loc}, is greater than the macroscopic value of the dielectric constant. This assumption is justified by the fact that the electron in a cavity "feels" the uncompensated C–H dipole moments of the surrounding molecules. The orientation of these dipoles is apparently responsible for the "blue" shift with time in the absorption spectrum of a captured electron in solid hydrocarbons (see Fig. 3).

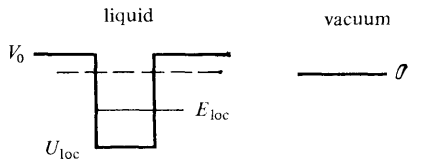


Figure 4. Energy diagram for an electron localised in a cavity. The broken line gives the energy level of the stationary electron in a vacuum, V_0 is the energy of the ground state of the quasi-free electron, and E_{loc} the energy of the localised state.

These proofs of the localisation of the electron in a cavity can only be regarded as indirect, however. It is not excluded that, because of the high dipole moment of individual C–H bonds (~ 0.4 D [67]), the electron is localised, for example, by a "fortuitous coincidence of rotational phases of neighbouring molecules" [11].

4. Some Models of Transfer

The observation of high values of the drift mobilities of an electron in liquid hydrocarbons led immediately to the suggestion that the unusual mobility of the electron in these media is due to the participation, in transfer processes, of an electron in a quasi-free state. Ideas on the high mobility of the quasi-free electron in a liquid had previously been introduced to explain the mobility of the electron in liquefied noble gases. For these media, a theory of the mobility of the quasi-free electron in a liquid was also developed in detail.

The quasi-free electron in monatomic liquids is regarded as a plane wave coherently scattered on atoms. This approach, used by Cohen and Lekner [68,69], was found to be fruitful for the estimation of the mobility of an electron in a weak electric field μ_0, and also in the interpretation of the temperature dependence $\mu_0(T)$ [70] and the dependence of the mobility on the electric field strength in liquid argon. The structure of the liquid was taken into account by means of a radial function of the interatomic distances, and the model potential of the interaction of the electron with an atom was the potential used in the calculation of the energy of the quasi-free electron. According to the theory [68,69]

$$\mu_0 = \frac{2}{3} e (2/\pi m k_B T)^{1/2} / n\sigma S(0), \qquad (4)$$

where $\sigma = 4\pi a^2$ is the cross-section of the elastic scattering of an electron on a sphere having a radius a, $S(0) = nk_BTx$, and x is the coefficient of isothermal compressibility of the liquid.

Fueki and coworkers [54] assumed that Eqn. (4) is also applicable for the mobility of a quasi-free electron in a molecular liquid, if the values obtained from the experimentally determined energies of the quasi-free electron according to Eqn. (3) are used for a. According to their estimates, $\mu_0 = 150 \pm 70$ cm^{2}V^{-1}s^{-1} for various liquids at $T \simeq 300$K. The value $\mu_0 \simeq 150$ cm^{2}V^{-1}s^{-1} for n-hexane, neopentane, and their mixtures is also given by a more rigorous calculation [71] based on a modified Cohen–Lekner theory for monatomic liquids [72].

The data in Table 1 show that the experimental values of the drift mobility of the excess electron in many molecular liquids is much smaller than the assumed values of μ_0 for the quasi-free electron. Moreover, in contrast to the calculated temperature dependence of the mobility of the quasi-free electron, $\mu_0 \sim T^{-3/2}$, for most liquid hydrocarbons the mobility of the excess electron has activational character, which usually indicates that a significant part is played by localised states. Thus the nature of the transfer of an excess electron is different for non-polar molecular liquids, polar liquids, and liquefied noble gases.

The mechanism of electron transfer in non-polar molecular liquids is not clear at present. A common feature of proposed models is the use of ideas on the distribution of the excess electrons between localised and quasi-free states. The following models of the transfer of an excess electron are examined in the literature, depending on the energy distribution of the traps and the mechanism of the liberation of the electron from the trap.

a) "Trap" model

In this model it is assumed that a quasi-free electron in a liquid is captured for a time interval τ_{loc} by structural traps, from which it can be liberated again by thermal excitation. In this case the measured mobility is the sum of the mobilities of the electron in the quasi-free state μ_0 and in the localised state μ_{loc} with allowance for the proportion of the time spent by the electron in these states, that is

$$\mu = \mu_0(1 - P) + \mu_{loc}P, \qquad (5)$$

where P is the probability that the electron is in the localised state.

For the simplest case where all the traps are identical, $P = \tau_{loc}/(\tau_0 + \tau_{loc})$, where τ_0 is the lifetime of the quasi-free electron before capture by the trap. If the mobility of the localised electron is neglected, and it is assumed that $\tau_{loc} = \nu^{-1}\exp(E/k_BT)$, where E is the activation energy of the liberation of the electron from the trap, ν is a frequency factor, and $\tau_0 \ll \tau_{loc}$, then Eqn. (5) gives an Arrhenius type of temperature dependence for the mobility: $\mu = \mu_0\tau_0\nu \exp(-E/k_BT)$. Comparison of the pre-exponential factor of this relationship and the experimental value for $\tau_0 \simeq \nu^{-1}$ leads to the conclusion that μ_0 is approximately the same, ~ 10^2 cm^{2}V^{-1}s^{-1}, for different liquids, in agreement with theoretical estimates.

The pre-exponential factor in the relationship $\mu = \mu_0' \exp(-E/k_BT)$ acquires a different physical significance if a distribution of the traps with respect to energy is assumed. Thus for a linear distribution from 0 to E, we have [29]:

$$\mu = \mu_0(1 + E_1/k_BT)\exp(-E_1/k_BT).$$

Comparison of this form of $\mu(T)$ relationship with the experimental relationship gives values of μ_0 which are smaller, the smaller μ. This change in μ_0 is more realistic, since liquids having a lower value of μ, as a rule,

have less "spherical" molecules, for which stronger scattering of the quasi-free electrons should be expected.

A more complex form of distribution of traps with respect to depth was used by Freeman and coworkers[73,74]. With the assumption that the distribution is Gaussian, and that the position of its maximum is linearly dependent on V_0, they obtained satisfactory agreement with the experimental $\mu(V_0)$ relationship for various hydrocarbons and tetramethylsilane (see Fig. 5).

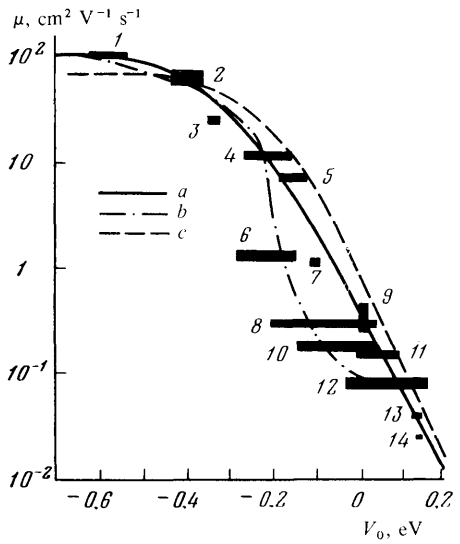


Figure 5. Dependence of the mobility of an excess electron on the energy of the quasi-free electron in a liquid at $T = 294 \pm 2$ K.[74] The lines give the calculated relationships: a) "trap" model with Gaussian distribution, b) "partial localisation" model, c) Kestner–Jortner model. Experimental data: 1) tetramethylsilane, 2) 2,2-dimethylpropane, 3) 2,2,4,4-tetramethylpentane, 4) 2,2-dimethylbutane, 5) iso-octane, 6) cyclopentane, 7) 2,3-dimethylbutane, 8) 2-methylpentane, 9) cyclohexane, 10) 3-methylpentane, 11) n-pentane, 12) n-hexane, 13) n-octane, 14) n-decane.

b) Fluctuation models

Schiller and coworkers[44,61] and Kestner and Jortner[75] tried to describe electron transfer with allowance for fluctuation processes in a liquid. A common feature of these approaches is the assumption that the mobility of the quasi-free electron $\mu_0 \simeq 10^2$ cm^{2}V^{-1}s^{-1} is approximately the same for all liquids.

In the "partial localisation" model[44,61], the probability that an electron is in a localised state P is related to a fluctuation in energy. Here, a central assumption is that there is "unrestrictedly fast exchange of energy between the electron and the molecules of the medium". In accordance with this assumption, the electron is in a quasi-free state if $E_{loc} + E > V_0 + \bar{E}$ (where E and $\bar{E}$ are the energy of the molecules forming the localised state of the electron, and its average value), and becomes localised when $E_{loc} + E < V_0 + \bar{E}$. In this case

$$P = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{V_0} \exp[-(E - E_{loc})^2/2\sigma^2]\, dE,$$

where σ^2 is the dispersion of the distribution with respect to E.

Satisfactory agreement with experimental data for V_0 and μ for $T \simeq 300$ K was obtained for $\sigma = 0.12$ eV (see Fig. 5). The order of magnitude of this value is consistent[44] with the known specific heat capacity of aliphatic hydrocarbons, $C_V = 50$ kcal mole^{-1}K^{-1}.

Kestner and Jortner[75] examined the mobility of a classical electron in a macroscopically non-uniform medium consisting of regions with different potentials of the interaction of the electron with the molecules (V). They assumed that these regions can be divided into two types, depending on the ratio of the values of E and V: "effectively conducting", with electron mobility μ_0, if $E > V$, and "poorly conducting", with electron mobility μ_1 of the order of ionic conductivity, if $E < V$. In this case[75], from the theory of electron transfer in disordered systems[75-78],

$$\mu = \mu_0\left(\frac{3}{2}C - \frac{1}{2}\right), \text{ for } C > 0.4,$$

where C is the volume fraction of the "effectively conducting" regions. Decrease in C from 0.4 to 0 is accompanied by a sharp decrease in μ to the value μ_1 at $C = 0$. To calculated C in various hydrocarbons it was assumed that the difference $\bar{V} - V_0$ (where $\bar{V}$ is the average value of V), and also the average value of E, are constant for all liquids.

Fig. 5 shows that this model is also consistent with experimental data for various liquids. As in other treatments, an exception is provided by the data on μ and V_0 for liquid methane.

c) "Hopping" model

For liquids having a relatively low electron mobility $\mu < 1$ cm^{2}V^{-1}s^{-1}, a transfer mechanism without conversion of the electron to a quasi-free state has also been proposed[79-81]: the electron remains in a localised state until a fluctuation produces in its proximity the same kind of trap, into which the electron "hops". In this case the activation energy of the mobility will be related to the processes of new trap formation and the "hopping" of the electron between traps. This so-called "hopping" mechanism of transfer is used to interpret the mobility of an electron in a large number of solids in which the electron has a low mobility[82], and also in polar[3] and weakly polar molecular liquids.

For liquid normal hydrocarbons at $T \simeq 300$ K, an indication of the hopping mechanism may be provided by data[36], according to which, with increase in the number of carbon atoms in the molecule $n_C > 7$, the mobility of the electron remains approximately constant (~ 0.04 cm^{2}V^{-1}s^{-1}), whereas V_0 continues to increase. In the transfer models examined above, this means that for $n_C > 7$, the quasi-free state does not make a contribution to the mobility, although its value still remains much greater than the mobility of ions.

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Thus the comparison of various models of the transfer of an excess electron in non-polar liquids with experiment involves the introduction of many simplifying assumptions. There are insufficient experimental data on $\mu(T)$ and $V_0(T)$ relationships to establish the transfer mechanism, since different models on the whole give satisfactory agreement with experiment. It is therefore necessary to introduce other experimental data. Information on the mobility of a quasi-free electron μ_0 and the density of the energy levels of an excess electron in a liquid $n(E)$ are particularly important. The use of one of the direct methods for determining μ_0—measurement of the Hall effect—is difficult for non-polar liquids, because of the low concentration of excess electrons, and has not yet given any results. The experimental determination of the $n(E)$ relationship can in principle be based on a study of the spectrum of the photo-detachment of an electron from a negative ion in a liquid, by analogy with the method of impurity photoconductivity for semiconductors. The possibility of recording photoconductivity due to the photo-detachment of an electron from negative ions in a non-polar liquid was recently demonstrated[83-85].

A fundamental difference between the mechanisms examined for the transfer of an excess electron in non-polar and polar liquids is the postulate that there is an appreciable probability that the electron is in a delocalised quasi-free state. This characteristic feature of non-polar liquids makes it possible to use direct experimental methods to study the reactivity of a delocalised electron—a short-lived species in condensed matter which is comparatively new in chemical kinetics.

III. CHEMICAL REACTIONS

The view that an excess electron has high reactivity arose in a study of the radiolysis of solutions of electron acceptors[86] long before the drift mobilities of the electron in "pure" liquids were measured. The estimation of the rate constants of the elementary reactions of an electron from the results of these studies was difficult, however, because of the complex kinetics of radiolysis processes. The use of thoroughly purified liquids in experiments made it possible to employ more direct methods to study the reactivity of an excess electron. One of the first direct methods was based on the determination of the lifetime of an excess electron in solution by recording the kinetics of the decrease in its optical absorption[56-58].

The method most widely used at present is pulse electrical conductivity, first used to determine the rate constants of the reactions of an electron by Fuochi and Freeman[19] and Yakovlev and coworkers[87].

Pulse Electrical Conductivity Method

In this method, the electrical conductivity of solutions is measured in a direct current circuit with the pulse generation of excess electrons in it (Fig. 6). The electrons are generated by the ionisation of solvent molecules by hard radiation (high-energy electrons, bremsstrahlung) or by two-quantum photo-ionisation of impurity molecules[24,88]. The ionisation of molecules in an amorphous substance leads to the formation of two types of electron-ion pair: pairs in which the electrons recombine with "their own" positive ion or an ion of "their own" tracks (so-called "primary" recombination), and pairs which avoid primary recombination or "free charges". The electrical conductivity method is convenient in that it is "sensitive" only to "free" electrons and ions, since the pairs taking part in the "primary" recombination do not make an overall contribution to the transfer of charge in a constant electric field. Processes involving "free" species can be described by the equations of ordinary homogeneous kinetics, and this simplifies considerably the analysis of the data obtained.

Since the mobility of an excess electron is much greater than the mobility of ions, excess electrons make the greatest contribution to the electrical conductivity with the condition that their concentration is comparable with the concentration of ions. These conditions are produced, for example, after the action of a short pulse of ionising radiation for times comparable with the lifetime of the excess electrons in solution. The rate of disappearance of the electrons in a solution is determined by several processes: recombination with positive ions in solution or at an electrode, and reactions with impurity molecules. Since electrical conductivity can be measured at very low concentrations of electrons ($\sim 10^8$ electron cm^{-3}) and large distances (~ 1 cm) between the electrodes, the experimental conditions can be selected so that one of these processes is the chief process.

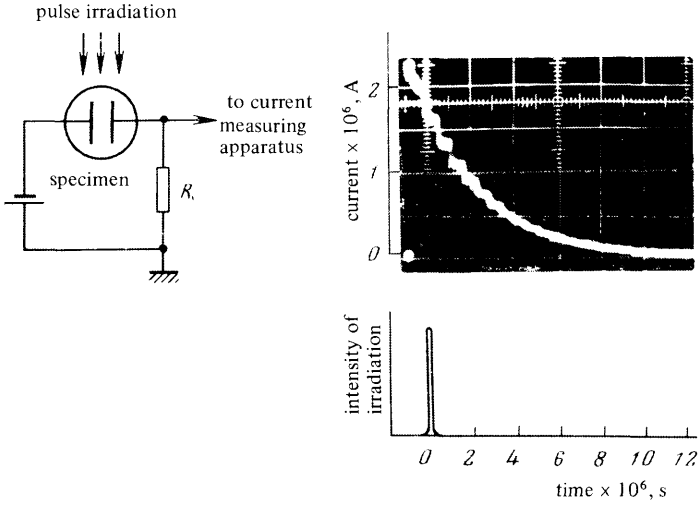


Figure 6. Measurement of the current of excess electrons in the pulse electrical conductivity method. The oscillogram of the current for a solution of pyrene in n-hexane at a concentration 1×10^{14} cm^{-3}.[28]

If the disappearance of the electrons takes place chiefly at the electrodes, it follows that for generation which is uniform throughout the volume, at $t = 0$, the decrease in the current will be described by a linear time dependence:

$$I \sim (1 - t/t_{\lim}) \text{ for } t < t_{\lim}.$$

Most of the data on the mobility of an excess electron have been obtained by recording relationships of this kind.

Under conditions in which the electrons disappear chiefly as a result of their capture by a molecule of an acceptor A

$$e^- + A \rightarrow A^-, \qquad (6)$$

when $[A] \gg [e^-]$, the decrease in the current will be described by an exponential relationship

$$I(t) \sim [e^-] \sim \exp(-t/\tau_3) \qquad (7)$$

where $\tau_3^{-1} = \Sigma k_i[A_i]$, $[e^-]$ is the concentration of excess electrons, k_i the rate constant of reaction (6), and $[A_i]$ the concentration of the acceptor i.

To illustrate this form of time dependence of the current, Fig. 6 gives the oscillogram of the current induced by a pulse of ionising radiation in a solution of pyrene in liquid hexane at a concentration of 1×10^{14} cm^{-3}. As follows from Eqn. (7), an increase in the concentration of the acceptor is accompanied by a decrease in the lifetime of the excess electron in solution (see for example Fig. 7). The rate constant of the capture reaction can be determined from the time of the exponential decrease in current if the duration of the generating pulse is sufficiently short, or from an analysis [29,87] of the more complex character of the change in current if $\tau_{pulse}^{-1} < k[A]$.

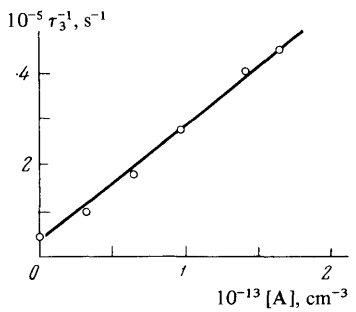


Figure 7. Plot of the reciprocal of the lifetime of an excess electron in liquid iso-octane solutions at 296 K against the pyrene concentration [17].

The electrical conductivity method has now been used to measure a large number of rate constants for the reactions of an excess electron in various liquid hydrocarbons. These reactions involve chiefly the capture of the excess electron by a neutral molecule of an acceptor (5) and the recombination of the electron with a positive ion

$$e^- + M^+ \rightarrow \text{(disappearance of } e^-\text{)}. \qquad (8)$$

2. Recombination Reaction

In the experimental study of reaction (8) in liquid hydrocarbons, it is usual to select conditions in which recombination is the chief process responsible for the disappearance of the excess electrons in the volume between the electrodes. In this case, data on the kinetics of the electrical conductivity, induced in the liquid by the pulse of ionising radiation, during [29,87,89] or after [89-91] the pulse make it possible to determine the ratio k_r/μ, where k_r is the recombination rate constant, and, when μ is known, to obtain k_r.

Fig. 8 gives the dependence of k_r on the mobility of the excess electron in various hydrocarbons and tetramethylsilane. For liquid hydrocarbons with an electron mobility $\mu < 10$ cm^{2}V^{-1}s^{-1}, the values of k_r, within the limits of accuracy of the measurements (~ 10%), satisfy the Langevin relationship

$$k_r = 4\pi e\mu/\varepsilon \qquad (9)$$

where ϵ is the dielectric constant. Eqn. (9) is based on the assumption that the reaction rate is limited by the diffusion of the recombining species, and that their path length before the loss of momentum l is shorter than the distance r_c at which the energy of the Coulombic interaction between the positive current and the electron is equal to k_BT (for non-polar liquids at $T \simeq 300$K, $r_c \simeq 300$ Å). For the excess electron, the last condition agrees with the assumed relatively low value of the mobility of the quasi-free electron ($\mu_0 \simeq 10^2$ cm^{2}V^{-1}s^{-1}), which corresponds to $l \simeq 60$ Å.

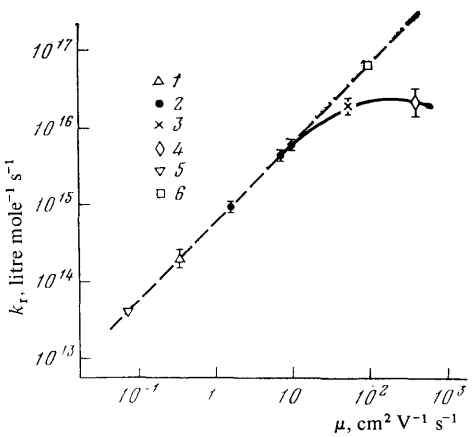


Figure 8. Dependence of the rate constant for electron-ion recombination on the mobility of an excess electron in non-polar liquids: 1) cyclohexane, 296 K [87]; 2) iso-octane, 200, 296, and 340 K [90]; 3) neopentane, 296 K [89]; 4) methane, 110 K [87]; 5,6) n-hexane, tetramethylsilane, 296 K. [29]

For liquids with a high excess electron mobility (neopentane, tetramethylsilane), the recombination rate constant has the highest values for bimolecular reactions in a liquid, ~ 10^{15} litre mole^{-1}s^{-1}. It is at present not clear whether the value of k_r for these liquids obeys the Langevin relationship: some data [19,29] give a ratio k_r/μ equal to the theoretical value, whereas other data [89] give values for this ratio which are smaller by factors of 1.5 for neopentane and 15 for liquid methane.

3. Capture Reactions

The reaction rate constants k for the capture of an electron in many non-polar liquids are now known for various acceptors. The following list of acceptors for which constants have been determined gives some idea of the range of studies carried out: O_2, [24,25,29,57,91-97] I_2, [92] CO_2, [91,93,95,98] N_2O, [33,84] SF_6, [33,99] CCl_4, [24,33,62,91-93,95,96] CH_3I, [29] C_2H_5Cl, [33] C_2H_5Br, [29,33] C_2HCl_3, [33] C_2H_3Cl, [33] biphenyl [24,96,91-93], pyrene [28,62,87,96,99], perylene [96], naphthalene [91], diphenylanthracene [93], and alcohols [91,100]. For "good"

electron acceptors, such as CCl_4, SF_6, N_2O, etc, in liquid hydrocarbons at $T \simeq 300$ K, the rate constants lie in the range 10^{12}–10^{14} litre mole^{-1}s^{-1}, that is they are 10–10^3 times greater than the rate constants of the analogous reactions of the hydrated electron.

Since in polar liquids the rate of the fast reactions of an electron are limited by the diffusion of the electron to the molecule of the acceptor, it is natural to relate the unusually high value of k primarily to the high mobility of the excess electron in non-polar liquids. The increase in k on going to liquids exhibiting a high mobility is also observed for non-polar liquids with a relatively low electron mobility (< 10 cm^{2}V^{-1}s^{-1}). For these liquids, the increase in reaction rate with increase in temperature characteristic of chemical reactions is also observed (Fig. 9). The dependence of k on T and μ for the capture of an electron by various acceptors in liquids with a high electron mobility is more unusual: k increases with decrease in T and decreases on going to liquids exhibiting a higher mobility.

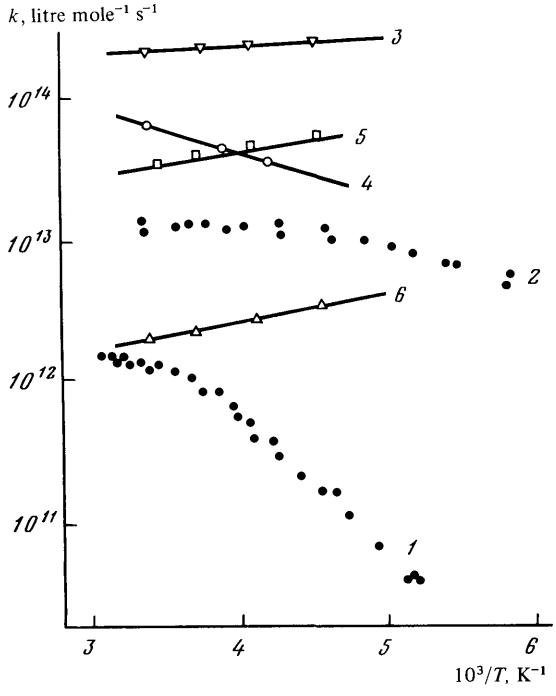


Figure 9. Temperature dependence of the rate constants for the capture of an excess electron by acceptor molecules: 1) and 2) pyrene in n-hexane[28] and iso-octane[17]; 3,4,5), and 6) SF_6, CCl_4, C_2HCl_3 and N_2O in tetramethylsilane[33].

The study of the mechanism of the capture of an electron in non-polar liquids has only begun. One of the tasks in this field is to determine the state, localised or quasi-free, in which the electron is captured by the acceptor molecule.

4. Role of the Localised and Quasi-Free Electron

With allowance for the two states of an excess electron in non-polar liquids—localised e^-_{loc} and quasi-free e^-_0—the kinetic scheme for the capture reaction can be represented in the form

$$\begin{array}{ccc} e^-_0 + A & \xrightarrow{k_0} & \\ \downarrow\uparrow & & A^-. \\ e^-_{loc} + A & \xrightarrow{k_{loc}} & \end{array}$$

From various estimates[101,102], the time required to establish the equilibrium $e^-_0 \rightleftharpoons e^-_{loc}$ is much shorter ($< 10^{-11}$ s) than the characteristic reaction times in the experimental determination of rate constants ($> 10^{-8}$ s), so that the values of the constants can be broken down into two components

$$k = k_{loc} P + k_0 (1 - P) \qquad (10)$$

where P is the probability of localisation, and k_{loc} and k_0 the reaction rate constants for the capture of an electron in localised and quasi-free states.

Which of these states makes the main contribution to the reaction rate? In the examination of this question for a qualitative estimate of the magnitude of P it is convenient to use the relationship

$$P = 1 - \mu/\mu_0, \qquad (11)$$

applicable for the trap model of the mobility of an excess electron, with the assumption that the mobility of the quasi-free electron is approximately the same for different liquids.

a) Reactions of a localised electron

It may be expected that for liquids for which the degree of localisation of an excess electron is high, so that its mobility is low, the localised state plays an important role in the chemical reactions of the excess electron.

For the capture of an electron by an O_2 molecule, which is a "poor" electron acceptor in non-polar liquids, this assumption is confirmed by the determination of the reaction rate constant $k(O_2)$ in various liquid hydrocarbons. The experimental data[94,97,103] show that the values of $k(O_2)$ are approximately constant for all liquids with low electron mobility studied (n-hexane, methylcyclohexane, cyclohexane, iso-octane), although for these liquids, the coefficient of diffusion of the electron and hence μ change by a factor of more than 70 (see Fig. 10). Eqns. (10) and (11) and the dependence of $k(O_2)$ on μ indicate that the main contribution to the reaction rate is made by the localised electron.

It may be assumed that the molecules of "good" acceptors in hydrocarbons having a low electron mobility also capture chiefly excess electrons in a localised state. In fact, the rate constants for the reactions of an electron with these acceptors are extremely high. For example, in n-hexane at $T \simeq 300$ K for SF_6, CO_2, pyrene, C_2H_5Br, etc., $k > 10^{12}$ litre mole^{-1}s^{-1}. If the contribution of localised electrons to the reaction rate were not the main contribution, then from Eqns. (10) and (11) it would be necessary, for these values of k, to assume values of $k_0 \simeq k/(1-P)$ which are too high. Thus in the "trap" model of transfer for $k = 10^{12}$ litre mole^{-1}s^{-1}, $\mu = 0.1$ cm^{2}V^{-1}s^{-1}, and $\mu_0 = 10^2$ cm^{2}V^{-1}s^{-1}, it would be necessary to assume that $k_0 = 1.2 \times 10^{15}$ litre mole^{-1}s^{-1}, which is greater than the limiting value for the reaction of a thermal electron in the gaseous phase $k_{lim} = \pi\lambda^2 v$, where $2\pi\lambda$ is the de Broglie wavelength, and v the velocity of the electron.

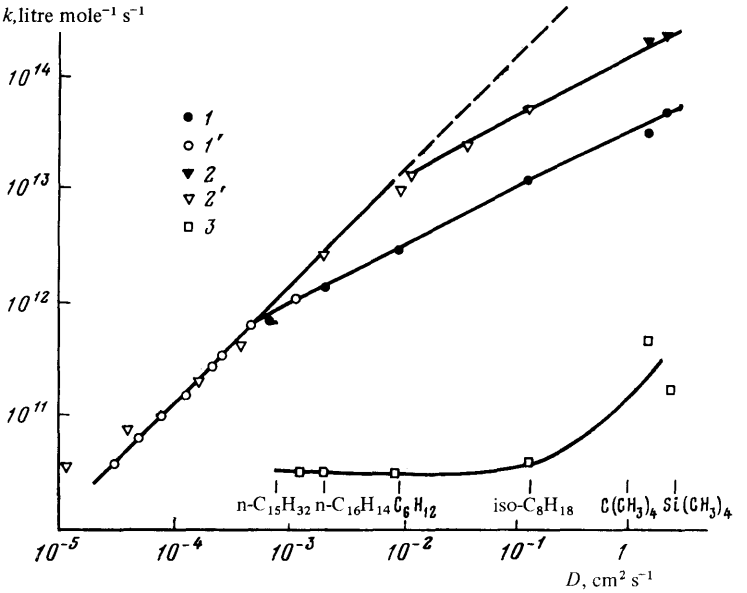


Figure 10. Relationship between the coefficient of diffusion of an excess electron and the reaction rate constants for the capture of the electron by the molecules of: 1,1′) pyrene in n-hexane, cyclohexane[28], iso-octane[17], pentadecane, and neopentane[135]; 2,2′) SF_6 in propane, ethane, n-hexane[99], and iso-octane[43]; 3) O_2 in methylcyclohexane, n-hexane, cyclohexane, iso-octane, neopentane, and tetramethylsilane[94,103]. The points *1*, *2*, and *3* relate to room temperature. The broken line corresponds to the relationship $k = 4\pi DR$ for $R = 16$ Å.

b) Reactions limited by diffusion

Fig. 10 gives data on the dependence of the rate constants for the capture of an electron by "good" acceptors on the diffusion coefficient of the excess electron D. The values of D were determined from the mobility of the electron using Einstein's relationship $D = kT\mu/e$. It can be seen that at values of $D < 10^{-3}$ cm^2s^{-1} (or $\mu < 0.1$ $cm^2V^{-1}s^{-1}$), the values of k are approximately proportional to D. This $k(D)$ relationship indicates that the reaction rate is limited by the diffusion of the excess electron to the acceptor molecule. For reactions of this type in non-polar liquids, the values of the radius of the reaction, characterising the distance between the species at the moment of electron transfer, are unusually high. Table 2 shows that the Debye–Smoluchowski equation for the radius of the reaction $R = k/4\pi\ (D + D_A)$, where $D_A \ll D$ is the diffusion coefficient of the molecule of the acceptor, gives values of 10–30 Å for the reactions of electron capture in liquid hydrocarbons, whereas for the diffusion-limited reactions of the solvated electron in water, R amounts to 2–3 Å.

The reason for the high values of the radii of reactions in liquid hydrocarbons is not clear. Estimates[28,104] show that it is difficult to attribute these values to the polarisation interaction of the excess electron and the acceptor molecule. If it is assumed that the electron is captured by the acceptor chiefly from the localised state, the high values of R can in principle be attributed to the large radius of the localised electron[28]. Radii of 20–30 Å for the localised electron are also postulated in the discussion of data on the mobility of an excess electron in liquid propane and pentane in strong electric fields[37].

It is possible, however, that the values obtained for R are effective values and are associated with a tunnel reaction mechanism.

Table 2. Radii of the reaction for the capture of an excess electron, calculated from the equation $R = ek/4\pi k_B T\mu$.

Acceptor	Liquid	T, K	μ, $cm^2\ V^{-1}\ s^{-1}$	k, litre $mole^{-1}\ s^{-1}$	R, Å
Pyrene	pentadecane	296	$3\cdot10^{-2}$ [135]	$6.6\cdot10^{10}$ [135]	11.6
SF_6	n-hexane	246	$1.8\cdot10^{-2}$ [99]	$3.8\cdot10^{11}$ [99]	13.5
C_2H_5Br	n-hexane	250	$2.3\cdot10^{-2}$ [28]	$5.0\cdot10^{11}$ [28]	13.8
Pyrene	n-hexane	250	$2.3\cdot10^{-2}$ [28]	$5.9\cdot10^{11}$ [28]	16.3
C_2HCl_3	n-hexane	253	$2.24\cdot10^{-2}$ [33]	$6.4\cdot10^{11}$ [33]	18
SF_6	propane	139	$3\cdot10^{-3}$ [99]	$7.2\cdot10^{10}$ [99]	26.5
SF_6	ethane	142	$4\cdot10^{-2}$ [99]	$1.0\cdot10^{12}$ [99]	27.5
SF_6	ethane	110	$1.3\cdot10^{-3}$ [99]	$5.0\cdot10^{11}$ [99]	55

c) Tunnel mechanism of capture

This mechanism has recently been frequently introduced in the discussion of the capture of an excess electron in polar liquids and solids[105–108]. With allowance for the diffusion of the electron and the acceptor molecule[108], the reaction rate constant for capture by a tunnel mechanism can be represented in the form $k = 4\pi DR_{eff}$, where the effective radius of the reaction is given by

$$R_{eff} = R_a + [1.15 + \ln(\alpha'/\beta^2 D)]/\beta, \qquad (12)$$

R_a is the sum of the radii of the acceptor molecule and the localised electron, α' a frequency factor, and $\beta = 2\hbar^{-1}[2m(V_0 - E_{loc})]^{1/2}$ is the attenuation factor of the wave function of the localised electron.

Eqn. (12) makes it possible to explain the high values of the radius of the reaction for the capture of an electron in liquid hydrocarbons. In fact, for these media the magnitude of the electron tunneling barrier $V_0 - E_{loc}$, equal in the simple trap transfer model to the activation energy of the mobility of the electron, is apparently less than 0.2 eV. If it is assumed that $\alpha' \simeq 10^{13}\ s^{-1}$, as is usually done for tunnel reactions in solid solutions [108], then for $V_0 - E_{loc} = 0.2$ eV and $D \simeq 10^{-4}\ cm^2 s^{-1}$, Eqn. (12) gives $R_{eff} \simeq 3R_a$. This estimate, for $R_a \simeq 5$ Å, shows qualitative agreement with the experimental data for the capture of an electron by "good" acceptors in liquid hydrocarbons characterised by low excess electron diffusion coefficients. It should be noted that the tunnel reactions of an electron in non-polar liquids differ from those in polar liquids in that the barrier to tunneling is appreciably smaller (for water, $V_0 - E_{loc} \simeq 1.5$ eV [108]). This means that, other conditions being equal, the rate of tunnel transfer from a distance of ~ 20 Å is $\geq 10^8$ times higher in liquid hydrocarbons than in water.

The assumption that the magnitude of the electron tunneling barrier in liquid hydrocarbons is approximately equal to the activation energy of the mobility of the electron also makes it possible to understand the order of magnitude of k for liquids with a high electron diffusion coefficient $D > 10^{-3}\ cm^2 s^{-1}$. In this range of values of D, the ratio k/D for many "good" acceptors decreases with increase in D (see for example Fig. 10), indicating that diffusion restrictions on the rate of reaction are removed. A qualitative estimate of the rate constant k' for the reaction not restricted by diffusion can be obtained by assuming that the concentration of localised electrons is independent of the distance r to the acceptor molecule. In this case

$$k' = \int_{R_a}^{\infty} 4\pi r^2 \omega(r)\, dr, \qquad (13)$$

where $\omega(r) \simeq 10\alpha' R^2 e^{-\beta(r-Ra)}/4r^2$ [108] is the probability of tunnel transfer, if the distance between the localised electron and the acceptor molecule is equal to r.

Eqn. (13) for $\alpha' \simeq 10^{13}\ s^{-1}$, $B_a = 5$ Å, and $V_0 - E_{loc} \simeq 0.1$ eV gives $k' \simeq 10^{13}$ litre $mole^{-1} s^{-1}$, which is of the same order of magnitude as the experimental values of k for acceptors such as N_2O, CCl_4, pyrene, biphenyl, and CO_2 in liquids with a high excess electron mobility (iso-octane, neopentane). At present, however, the tunnel mechanism of capture is not unambiguous for non-polar liquids with a high excess electron mobility. It is possible that as a consequence of the low degree of localisation of the electron in these liquids, the acceptor captures the electron in a quasi-free state.

d) Reactions of the quasi-free electron

The chemical reactions of a delocalised electron in condensed media have recently been introduced to interpret fast reactions involving electrons formed in the tracks of charged particles. It is assumed that in polar liquids, the delocalised state of the track electron, often called "dry", precedes the formation of the solvated electron. Attempts to determine the reactivity of "dry" electrons have been based on the study of the influence of an acceptor on the yield of solvated electrons [109-114] or the probability of positronium formation in a positron track [115-117]. Because of the short lifetime of the "dry" electron in polar liquids and the complex nature of the kinetics of track processes, the use of these methods to study the elementary reactions of a delocalised electron presents considerable difficulties. In the case of non-polar liquids, it is possible to use for this purpose a more direct method based on the study of the reactions of excess electrons which have avoided track recombination. The use of this method for electrons in liquefied noble gases, for which the quasi-free state of an electron is stable, has shown [118,119] that the reaction rate constants for the capture of a quasi-free electron may reach extremely high values (for example, 3×10^{14} litre × $mole^{-1} s^{-1}$ for SF_6 in liquid xenon).

In non-polar molecular liquids, the study of the reactions of the quasi-free electron is complicated by the fact that the reactions of the excess electron in the localised state are also possible. In the case of the reactions of an excess electron not restricted by diffusion, the reaction rate constant for the capture of a quasi-free electron k_0 can be estimated from Eqns. (10) and (11) and the experimental $k(\mu)$ relationship for different liquids. This approach has been used [94,103] to study the reaction

$$e_0^- + O_2 \rightarrow O_2^-. \qquad (14)$$

As already noted, the reaction rate constant for the capture of an excess electron by an O_2 molecule is approximately the same for different liquid hydrocarbons having an electron mobility $\mu < 10\ cm^2 V^{-1} s^{-1}$. On going to liquids with high values of μ (neopentane, tetramethylsilane), the value of the constant increases considerably (see Fig. 10). This increase can be attributed to an increase in the contribution of the quasi-free electron e_0^- to the reaction rate. The values obtained with this assumption for the rate constant of reaction (14), $k \simeq 3 \times 10^{11}$ litre × $mole^{-1} s^{-1}$ at 300 K, and the activation energy, < 0.01 eV [94,103], agree with the results of the study of the capture of a quasi-free electron in liquid krypton and argon [119].

The assumption that the capture of an electron in a quasi-free state predominates in liquids characterised by a high electron mobility makes it possible to explain the negative activation energy for various reactions, and also the existence of a maximum on the curve giving the dependence of k on the energy of the quasi-free electron (see Fig. 11). For the interpretation of these results, existing views on the reaction of low-energy electrons with molecules in the gaseous phase have proved useful.

e) Comparison with gas-phase data

At present, only the first attempts [33,103,120,121] have been made to examine theoretically the capture of a quasi-free electron by an acceptor molecule in a liquid. These attempts are based on the assumption that the mechanism of these reactions is analogous to that of the reactions of ar electron with molecules in the gaseous phase. In the last case it is usually assumed [123,124] that for an electron with a low energy (< 3 eV) the reaction takes place in two stages:

$$\text{I.}\quad e_0^- + A \underset{\tau_1^{-1}}{\overset{k'}{\rightleftarrows}} (A^-)^*$$

$$\text{II.}\quad (A^-)^* \longrightarrow \begin{cases} \rightarrow A^- \\ \rightarrow B^- + D \end{cases}.$$

Stage I is the formation of an intermediate vibrationally excited ion $(A^-)^*$ (τ_1 is the lifetime of the ion with respect to self-ionisation), and stage II is the stabilisation of the

ion as a result of collision with a third particle or dissociation. For the first stage of the reaction, the difference from the gaseous phase is that in the liquid, the term of the initial state (acceptor molecule + delocalised electron) is displaced along the energy scale by an amount V_0, and the term of the final state (the negative ion of the acceptor) is displaced by an amount equal to the energy P_- of the electronic polarisation of the molecules of the medium by the negative ion, situated in the same environment as the acceptor molecule before electron capture. Thus in the gaseous phase the formation of various states of the negative ion takes place at an electron energy ϵ_m, whereas in the liquid this requires the kinetic energy of the quasi-free electron

$$\tilde{\epsilon}_m = -V_0 + P_- + \epsilon_m \ . \qquad (15)$$

For many negative ions in non-polar liquids, $-P_- = 1.5 \pm 0.8$ eV.[85,121] Thus a thermalised quasi-free electron in a liquid with $-0.6 < V_0 < +0.2$ eV may lead to the formation of the same states of the negative ion as an electron in the gas with an energy 0.3–2.5 eV.

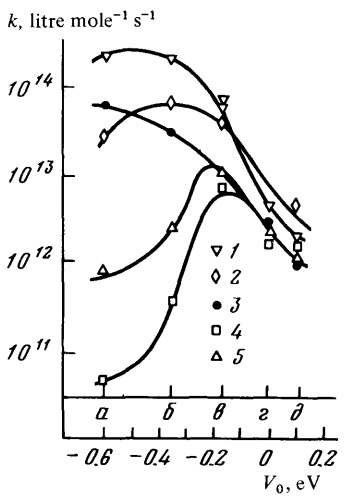


Figure 11. Relationship between the energy of a quasi-free electron V_0 and the reaction rate constants for the capture of an excess electron by molecules of SF_6 (1), C_2HCl_3 (2), CCl_4 (3), C_2H_5Br (4), N_2O (5).[33] The values of k and V_0 were measured for the following liquids at room temperature: tetramethylsilane (a), neopentane (b), isooctane (c), cyclohexane (d), and n-hexane (e).

In this approach it is possible to attribute the maxima on the curve giving the dependence of k on V_0 (see Fig. 11) to the fact that the thermal energy of the quasi-free electron corresponds to a maximum cross-section for the formation of the intermediate ion, that is $3/2k_BT = \epsilon_m - V_0 + P_-$. For the C_2HCl_3 molecule, for example, $\epsilon_m = 0.4$ eV,[125] so that for $P_- \simeq -0.7$ eV,[33] a maximum capture cross-section should be expected at $V_0 \simeq -0.3$ eV, in agreement with the data in Fig. 11. Since for $3/2k_BT > \epsilon_m - V_0 + P_-$ a decrease in V_0 leads to deterioration in the resonance conditions, it is also possible to understand the decrease, unusual for classical diffusion theory, in the reaction rate constant on going to liquids with a higher electron mobility and hence a lower value of V_0. A decrease in k with decrease in V_0 is characteristic of not only C_2HCl_3 but also other acceptors: N_2O, CO_2, and C_2H_5Br, the molecules of which have a negative electron affinity in the gaseous phase[33,120].

The assumption that the mechanism of the capture of a quasi-free electron is analogous to that of the reaction in the gas also makes it possible to explain the negative activation energies for various reactions involving the capture of an excess electron in a non-polar liquid (see Fig. 9). In fact, for $3/2k_BT > \epsilon_m - V_0 + P_-$, decrease in temperature leads to an improvement in the conditions for resonance, since V_0 increases (see Fig. 2). Moreover, an estimate[103] of the absolute magnitude of the rate constant of the reaction $e_0^- + O_2 \rightarrow O_2^-$, based on gas-phase data on the cross-section for the formation of the intermediate ion O_2^-, gives satisfactory agreement between experiment and the activation energy and the order of magnitude of k.

5. Excess Electrons in the Primary Processes of Photolysis and Radiolysis

Recent quantitative data on the mobility and reactivity of an excess electron are extending considerably the possibilities provided by the analysis of the kinetics of various electronic processes in molecular liquids. Of greatest interest among these, judging from the number of published papers, are the primary photochemical and radiation-chemical processes in liquid solutions.

As already noted, the ionisation of molecules in a liquid leads to the formation of two types of electron–ion pair: pairs involved in "primary recombination", and pairs which avoid this recombination, or "free" charges. In the formation of electron–ion pairs under the influence of ionising radiation[126,127] or as a result of two-quantum ionisation[128], only a small fraction of the electrons become "free" (from 2% in liquid n-hexane to 20% in neopentane). For many-component systems, the direction of the chemical processes taking place after ionisation is determined to a great extent by the proportion of electrons captured by acceptor molecules before recombination.

The theoretical approaches used to describe the kinetics of "primary" recombination in the presence of electron acceptors are based on the theories of diffusion and drift in the Coulombic field of the electrons, which are regarded as classical charged particles, in thermal equilibrium with the medium[129–132]. The most widely accepted theory at present is that proposed by Hummel[130] and subsequently developed for radiation problems[132–134].

This theory examines the distribution with respect to lifetimes $n(t)$ of the number of electrons undergoing "primary" recombination in the pure solvent. It is assumed that among these electrons, the proportion of electrons recombining with a positive ion in the presence of an acceptor is given by

$$N = \int_0^\infty n(t)\, e^{-k[A]t}\, dt, \qquad (16)$$

where k is the rate constant of the capture reaction. In this approach, the moment of time corresponding to the recombination of the negative ion A^- formed by the capture of an electron by the acceptor can be expressed simply in terms of the lifetime of the electron in the pure solvent $t(e^-)$ and the ratio of the drift mobilities of the electron and the ion r_d. In fact, for classical particles, the rate of

recombination is inversely proportional to the sum of their mobilities, so that $t(A^-) = t_c + [t(e^-) - t_c]\gamma_d$, where t_c is the time of electron capture, and $t(A^-)$ the time of ion recombination. A knowledge of the distribution of the mobilities and the rate constants of the charged species makes it possible to obtain a complete description of the kinetics of "primary" recombination.

Eqn. (16), which is the Laplace transform for the function $n(t)$, makes it possible to establish the distribution of electrons with respect to lifetime up to the moment of recombination from the experimental dependence of N on [A]. In the case of the radiolysis of non-polar solutions, for the determination of $N([A])$ in the Hummel–Schuler theory, the empirical dependence of the yield of the ions A^- on the concentration of the acceptor[86] is used:

$$G(A^-) = G_{fi} + G_{prim}\frac{(\alpha[A])^{1/2}}{1+(\alpha[A])^{1/2}}, \qquad (17)$$

where G_{fi} is the yield of "free" ions, $G_{prim} \simeq 4$ is a parameter interpreted as the yield of electrons taking part in "primary" recombination, and α a coefficient which depends on the properties of the acceptor and the solvent. From Eqn. (17) it follows that

$$1 - N = \frac{(\alpha[A])^{1/2}}{1+(\alpha[A])^{1/2}}. \qquad (18)$$

According to a calculation[132] based on Eqns. (16) and (18), $\alpha = k/\lambda$, where λ is a coefficient characterising the rate of the "primary" recombination, and the distribution function has the form:

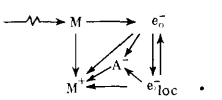
$$n(t) = -\frac{d}{dt}\left[e^{\lambda t}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\sqrt{\lambda t}} e^{-x^2}dx\right)\right]. \qquad (19)$$

The value of λ can be estimated from experimental data for k and α. For example, for liquid cyclohexane at $T \simeq 300$ K, this estimate gives $\lambda \simeq 2 \times 10^{11}$ s^{-1},[33] which for $n(t)$ of form (19) corresponds to a time of recombination of 50% of the electrons $t_{1/2} = 0.6\,\lambda^{-1} = 3 \times 10^{-12}$ s.

Values recently obtained for k and the mobility of an excess electron show satisfactory agreement[135-139] within the framework of the diffusion models with data for the yield of negative ions in liquids with a relatively low electron mobility ($\mu < 10$ cm^{2}V^{-1}s^{-1}). Moreover, the results of the study of the $n(t)$ relationship, obtained by measuring the optical density of electrons[56,58], lead to $\int_t n(t)dt \sim t^{-1/2}$, which corresponds to Eqn. (19) for $t \gg \lambda^{-1}$. It has also been established that diffusion theory effectively described the kinetics of the decrease in the quantity of biphenyl ions formed in the nanosecond radiolysis of a solution of biphenyl in cyclohexane[140].

In the interpretation of the results in all these cases, the electron was regarded as a classical particle with a mobility equal to the drift mobility of the excess electron. In relation to recently discussed models of the movement of an electron in a non-polar liquid, which assume the participation of quasi-free and localised states of the electron, these ideas can be justified if two conditions are satisfied. Firstly, the free path l of the quasi-free electron must be less than the characteristic dimension of the problem being considered[141]. In the study of the kinetics of "primary" recombination, this dimension is the distance from the positive ion on which the electron is thermalised. For most excess electrons generated by ionising radiation in a non-polar liquid, this distance is 60–100 Å.[40] In photo-ionisation it may be even smaller (~ 30 Å[50]). Since the assumed value of the mobility of a quasi-free electron, $\sim 10^2$ cm^{2}V^{-1}s^{-1}, corresponds to $l \simeq 60$ Å, this condition is apparently fulfilled only for a small proportion of the excess electrons, thermalised at distances greater than the average thermalisation length. Secondly, the processes being considered must be sufficiently slow, compared with the time taken for equilibrium to be established between the quasi-free and localised states, since otherwise it is not possible to use the drift mobility to determine the rate of recombination of the electron, and the constant k to calculate the probability of the capture of an electron by an acceptor molecule.

In the more general case it is necessary to consider a scheme of "primary" recombination including processes involving the capture and recombination of a quasi-free electron before localisation:



In contrast to diffusion models, the description of the kinetics of the processes in this scheme requires data on the spatial and time distribution separately for both the quasi-free e_0 and localised e^-_{loc} electrons and the probabilities of their reactions with an acceptor molecule.

The satisfactory agreement, described above, between diffusion theories and experiment is apparently related to the fact that in all cases the processes considered were comparatively slow, with characteristic times greater than the lifetime of the localised electron. For cyclohexane, for example, the lifetime of an electron in a localised state is $\tau_{loc} \simeq 10^{-10}$ s at $T = 300$ K, if it is assumed that the energy of liberation of an electron from a structural trap in the liquid is equal to the activation energy of the mobility of the electron (0.17 eV[21]), and the frequency factor is $\nu \simeq 10^{13}$ s^{-1}. Thus by using nanosecond technique for kinetic studies of "primary" recombination in this liquid, it is possible to "feel" only those electrons which are captured many times by the traps. This conclusion also applies to the method of studying kinetics based on an analysis of the concentration dependence of the yield of the negative ions of the electron acceptors, at concentrations of the acceptor $[A] \leq 10^{-2}$ M, for which $k[A] < \tau^{-1}_{loc}$.

At acceptor concentrations $[A] \simeq \tau^{-1}_{loc} k^{-1}$, the acceptor will efficiently capture electrons which have undergone a small number of transitions between localised states. The value of the drift mobility of the electron cannot be used to describe the motion of these electrons and hence the kinetics of the recombination of the negative ions for which they are the precursors.

At even higher acceptor concentrations, the quasi-free electron may be captured by an acceptor immediately after ionisation, before it is thermalised or localised in a structural trap. This possibility at $[A] > 10^{-1}$ M is assumed, for example, in the discussion of the influence of electron acceptors on the yield of "free" ions[142] or on the probability of positronium formation in a positron track[116,117]. In this case the equilibrium distribution of the excess electron with respect to states is broken down, so that Eqn. (16) becomes inapplicable.

Thus the determination of the distribution function of the electrons $n(t)$ from the experimental dependence of $G(A^-)$ on [A] at $t < \tau_{loc}$ can hardly be reliable. This possibly explains why the time of the "primary" recombination of 50% of the electrons in liquid cyclohexane, estimated by this method (3×10^{-12} s), was found to be shorter than the

lifetime of the electron in a localised state (10^{-10} s), assumed from data on the mobility of the excess electron.

Thus the use of the diffusion approach in the analysis of electron processes following ionisation is justified only for processes with a characteristic time $\gg \tau_{loc}$. In the examination of processes involving an excess electron for times $< \tau_{loc}$, the data at present available on the reactivity and mobility of the excess electron are inadequate. It is necessary to have data on the dynamics of the thermalisation and localisation of the electron, on the proportion of electrons recombining with a "free" ion without the stage involving localisation in the liquid, and on the distribution of these electrons with respect to their lifetime before recombination. Direct quantitative data of this kind will apparently be obtained in the near future by the use of nanosecond techniques.

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Mass Spectrometry with Chemical Ionisation

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The fundamental processes occurring in the interaction of organic molecules with Brønsted and/or Lewis acids in the gas phase are discussed and the fragmentation of the principal classes of organic compounds initiated by chemical ionisation is examined. It is shown that the unique advantages of mass-spectrometry with chemical ionisation are manifested most strikingly in structural studies of complex natural and synthetic products with labile bonds.
The bibliography includes 107 references.

CONTENTS

I. Introduction 631
II. Main definitions, principles, and relations 632
III. Mass spectra of the chemical ionisation of different classes of organic compounds 633
IV. Mass spectrometry of negative ions with chemical ionisation. The S_N2 reaction in the gas phase 641

I. INTRODUCTION

The origins of the development of chemical ionisation (CI) must be sought in experiments with molecular beams and the study of ion–molecule reactions in the gas phase†. The bibliography of the research on ion–molecule reactions during 1900–1966 includes more than 430 references and half of these cover the period since 1962.[4] In 1952 Tal'roze and Lyubimova detected for the first time the CH_5^+ ion (the methonium ion) in the ionisation chamber of a mass-spectrometer[5]. The first mass spectra with chemical ionisation[6,7] (CIM-spectra) were obtained in 1965 by Munson and Field on the Esso chemical physics mass-spectrometer[6,7]. These were the spectra of C_2H_6, n-C_3H_8, H_2O, and NH_3.[6,7] However, the application of CI in analytical chemistry began in 1966.[8] The extensive incorporation of CI in practical research is associated with the modification in 1969 of the two most common high-resolution mass-spectrometers—AEI MS-902 [9] and Du Pont/CEC 21-110C.[10] The development of a combined analytical method based on a gas–liquid chromatograph and a mass-spectrometer with chemical ionisation (GLC/MS-CI [11]) led to the intensive employment of CI in studies on complex biochemical mixtures. The application of CI in physicochemical research is associated with the development by Field of a method for the estimation of the kinetic parameters of reactions involving the molecular decomposition of protonated molecular ions and a method for the investigation of the kinetic parameters of reversible reactions[12] and also to some extent with the development of a procedure for the estimation of the proton affinities of the test compounds[13]. Finally the development of the CI-mass-spectrometry of negative ions made it possible to investigate S_N2 reactions in the gas phase[14-17].

The Essential Features of Chemical Ionisation‡. Problems of Nomenclature

At low pressures (10^{-5} mmHg and below) the ionisation of molecules and unimolecular decomposition of the ions formed take place in the ionisation chamber of the mass-spectrometer under electron impact. For example, the following reactions take place in methane:

$$CH_4 + e \rightarrow CH_4^{+\cdot}, CH_3^+, CH_2^{+\cdot}, CH^+, \ldots + 2e \quad . \tag{1}$$

The ions formed under these conditions are primary and the spectrum recorded is the primary spectrum of the reactant gas.

With increase of pressure, ion–molecule reactions between the primary ions and neutral molecules begin to occur together with reactions of type (1). For example, the following reactions take place in methane[5,21]:

$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^+ + CH_3^{\cdot}, \tag{2}$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2, \tag{3}$$

$$CH_2^{+\cdot} + CH_4 \rightarrow C_2H_4^{+\cdot} + H_2, \tag{4}$$

$$CH_2^{+\cdot} + CH_4 \rightarrow C_2H_3^+ + H_2 + H^{\cdot}, \tag{5}$$

$$C_2H_3^+ + CH_4 \rightarrow C_3H_5^+ + H_2 \cdot \tag{6}$$

The ions formed under these conditions can be secondary or reagent ions and the spectrum recorded is the secondary spectrum of the reagent gas. Reactions (2)–(6) assume a significant importance at pressures above 0.01 mmHg and are characterised by extremely high rate constants (virtually each collision of a primary ion with a neutral molecule terminates in reaction). At 1 mmHg the CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions constitute 95% of the overall ionic current (48, 51, and 6% respectively)[4]. It is significant that the secondary ions as a rule do not interact

† The term chemoionisation (chemiionisation) appeared in the literature in 1949 [1] and is used (in contrast to CI) to denote a wide variety of reactions between neutral atoms and molecules, leading to the formation of electrons and ions[2,3].

‡ In principle, chemical ionisation can be achieved in at least three ways[18]: (1) on double mass-spectrometers (tandems); (2) by ionic cyclotron resonance; (3) using the high-pressure mass-spectrometric technique. In the present review this problem is discussed only in relation to the use of the high-pressure mass-spectrometric technique. The experimental aspect of CI is examined in other reviews[19,20].

(or interact very slowly) with the neutral molecules of the reagent gas, i.e. the ratios of the intensities of the signals of the secondary ions in a specified range of reactant gas pressures do not vary to a first approximation (in the case of methane the $C_2H_3^+$ ion is an exception).

If approximately 0.1% of the test substance (the *substrate*) is added to the recent gas, then secondary ions interact with the substrate molecules, a proton or a hydride ion being transferred, i.e. they act like Brønsted and/or Lewis acids [reactions (7) and (8)]. The BH_2^+ ion will henceforth be referred to as the *protonated molecular ion* or the quasi-molecular ion $[M + H]^+$ and the ion B^+ will be called a *quasi-molecular ion* $[M - H]^+$. The BH_2^+ and B^+ ions can decompose under certain conditions [reactions (9)–(11)]. Reactions (12)–(14) illustrate the formation of cluster-ions§. The ions on the right-hand side of Eqn.(7)–(14) form the CH_4 spectrum of BH. The interaction with electrons and with the primary ions of the substrate molecules can be neglected in view of the low concentrations of the latter:

$$BH + CH_5^+ (C_2H_5^+) \rightarrow BH_2^+ + CH_4 (C_2H_4) \quad , \tag{7}$$

$$BH + C_2H_5^+ (CH_5^+) \rightarrow B^+ + C_2H_6 (CH_4 + H_2) \quad , \tag{8}$$

$$BH_2^+ \rightarrow B^+ + H_2 \quad , \tag{9}$$

$$BH_2^+ \rightarrow A_i^+ + B_i \quad , \tag{10}$$

$$B^+ \rightarrow A_{i'}^+ + B_{i'} \quad , \tag{11}$$

$$BH + C_2H_5^+ \rightarrow BH \cdot C_2H_5^+ \quad , \tag{12}$$

$$BH + C_3H_5^+ \rightarrow BH \cdot C_3H_5^+ \quad , \tag{13}$$

$$BH + BH_2^+ \rightarrow (BH)_2 H^+ \quad . \tag{14}$$

II. MAIN DEFINITIONS, PRINCIPLES, AND RELATIONS

One must distinguish two most common types of interactions occurring during CI: (1) acid–base interactions and (2) interactions of the oxidation-reduction type. The ions formed in the former and latter cases have even and odd numbers of electrons respectively. Examples of interactions of the first type are provided by reactions (7)–(14). Reactions of the second type are charge-transfer processes:

$$M + X^{+\cdot} \rightarrow M^{+\cdot} + X, \tag{15}$$

where M is a substrate molecule and X = He, Ne, Ar, Xe, NO, N_2, etc. The internal energy of the molecules ion formed (E_{in}) is equal in the given case to the difference between the recombination energy $RE(X^{\cdot})$ of the reagent ion in the gas phase and the ionisation potential IP(M) of the substrate molecule[23]: $E_{in} = RE(X^{\cdot}) - IP(M)$. Exact knowledge of this quantity can prove extremely useful in theoretical studies. Charge transfer between the substrate molecule and reagent ion can be observed (and is indeed observed) for reagent gases of the first type (see Table) against the background of acid–base interactions if the recombination energy of reactant ions is fairly large. In the CH_4 spectra a phenomenon of similar kind has been observed for the reagent ions $C_2H_4^+$, $C_2H_5^+$ [29] and CH_5^+.[30]

§ The presence of cluster ion peaks in the CIM-spectrum greatly simplifies the solution of the problem of the identification of the peak due to the quasi-molecular ion $[M + H]^+$.[22]

Only processes leading to the formation of ions with an even number of electrons will be examined in detail in the present review. The following generalisations are applicable to them.

1. In contrast to photoionisation and ionisation by electrons, CI processes occur with an equilibrium of atomic nuclei and electrons (in the ground state).
2. The internal energy of the ions formed is much lower than in ionisation by electrons and approaches the energy of ions formed in ion–molecule reactions in the condensed phase.
3. The ions formed in CI interact with gas molecules, transferring the excess energy until the occurrence of thermal equilibrium; it is therefore assumed that the range of ionic energies is fairly narrow and corresponds approximately to the range of energies in the usual chemical reactions in solution[29,31]¶.

The reagent gases used for chemical ionisation [PA(X) is the proton affinity and $RE(X^+)$ (eV) the recombination energy].

Acid–base reactions (type 1) (Refs.22–27)			Charge transfer (type 2) (Ref.28)		
gas (X)	reagent ions	PA(X), kcal mole^{-1}	gas	principal ion	$RE(X^+)$, eV
H_2	H_3^+	100	He	$He^{+\cdot}$	24.6
CH_4	CH_5^+	127	Ne	$Ne^{+\cdot}$	21.6; 21.7
CH_4	$C_2H_5^+$	159	Ar	$Ar^{+\cdot}$	15.8; 15.9
CH_4	$C_3H_5^+$	—	Ar	Ar^{2+}	~24
C_2H_4	$C_2H_5^+$	160	N_2	$N_2^{+\cdot}$	15.3
iso-C_4H_{10}	t-$C_4H_9^+$	195	N_2	N^+ or $(N_2)^{2+}$	
iso-C_5H_{12}	t-$C_5H_{11}^+$	—	N_2	$N_4^{+\cdot}$	
C_6H_{14}	$C_6H_{13}^+$	—	Kr	$Kr^{+\cdot}$	14.0; 14.7
C_8H_{18}	$C_8H_{17}^+$	—	Kr	Kr^{2+}	~21
C_8H_{18}	$C_6H_{13}^+$	—	CO	$CO^{+\cdot}$	14.0
C_8H_{18}	$C_5H_{11}^+$	—	CO	$(CO)_2^{+\cdot}$	11–12
H_2O	H_3O^+	165	CO_2	$CO_2^{+\cdot}$	13.8
H_2S	H_3S^+	170	CO_2	$(CO)_2^{2+}$	—
CH_3OH	$CH_3OH_2^+$	182	CO_2	$O_2^{+\cdot}$	9.7–17.0
NH_3	NH_4^+	207	Xe	$Xe^{+\cdot}$	12.1–13.4
CH_3NH_2	$CH_3NH_3^+$	216	Xe	Xe^{2+}	18–20
$(CH_3)_2NH$	$(CH_3)_2NH_2^+$	222	O_2	$O_2^{+\cdot}$	9.7–17.0
$(CH_3)_3N$	$(CH_3)_3NH^+$	227	CF_4	CF_3^+	IP=9.17
$(CH_3)_4Si$	$(CH_3)_3Si^+$	—	NO	NO^+	9.25 (8.3)

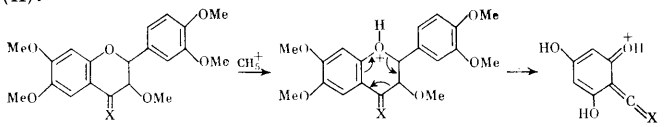
All three factors determine the specific nature of even-electron CIM-spectra, namely (a) the degree of fragmentation is smaller than in ionisation by electrons, (b) the peaks of quasi-molecular ions $[M + H]^+$ and /or $[M - H]^+$ are usually very intense, and (c) fragment ions giving rise to fairly intense peaks and having masses close to that of the quasi-molecular ions are as a rule identified in the CIM-spectrum.

¶ However, one must bear in mind that, although comparison with behaviour in solution is attractive and fruitful, it suffers from certain limitations due to the following three factors: (1) the reaction time in CI is much shorter (approximately 10^{-6} s); (2) the energies of the ions are somewhat higher; (3) there is no solvation.

It is noteworthy that complex molecules, when the latter can be transferred to the gas phase without decomposition, can suffer less fragmentation than relatively simple ions, in view of the greater possibility of a rapid redistribution of the vibrational energy of the ions among the internal degrees of freedom under conditions where the local excess energy is still insufficient for bond dissociation[32].

It is assumed that in a non-polar or weakly polar molecule fragmentation occurs as a result of random attack by the reagent ion on a particular section of the molecule, but fragmentation is as a rule localised at the site of attack (see, however, Foltz and Fentiman[33]). It has been shown that the presence of a static dipole in the molecule appreciably increases the cross-section of ion–molecule reactions[34], so that it is reasonable to suppose that the greatest number of effective collisions of the reactant ions with substrate molecules involve functional groups[29]. When the molecule contains several functional groups, the attack occurs to some extent via all the functional groups and the CIM-spectrum can be usually regarded as a combination of ions formed as a result of attack via each functional group separately. Such behaviour can be accounted for by the fact that the ions formed in CI have a relatively low energy and the migration of the charge in an even-electron ion usually requires the simultaneous migration of atoms or a group of atoms in the ion.

It follows from the foregoing considerations that the fragmentation of a polyfunctional compound with an increased lability of the molecule can nevertheless lead to the appearance of an intense peak of the $[M + H]^+$ ion when the molecule contains at least one group which "leaves with difficulty". For example the presence of the carbonyl group, which is readily protonated with formation of a stable ion, in the molecule of the flavanoid 2,3-*trans*-3,5,7,3′,4′-pentamethoxyflavanone (I) leads to an appreciable increase of the stability of the ion $[M + H]^+$ compared with 2,3-*cis*-3,5,7,3′,4′-pentamethoxyflavan (II):[35,36]



(I): X=O, $[M + H]^+$ (52%)*, *m/e* 181 (16%); (II): X=H_2, $[M + H]^+$ (18%), *m/e* 167 (44%)*. (16)

An analogous example with fragmentation of 5α-androstan-17β-ol (III) and 17β-hydroxy-5α-androstan-3-one (IV), for which the $[M + H]^+$ peak intensities are 3.9 and 50.2% respectively, has been published[20]†. The low intensity of the peak due to the ion $[M + H]^+$ derived from compound (III) is due to the great ease of the elimination of the OH group as H_2O following its protonation. The sharp increase of the stability of the ion $[M + H]^+$ derived from compound (IV) is associated, as in the previous example, with the presence of the carbonyl group.

The tendency of various functional groups to be eliminated has not been subjected to a systematic comparative study, but it is known, for example, that NH_2 is eliminated in the form of NH_3 with difficulty, halogens are eliminated as HHal, and the acetoxy-group is eliminated as CH_3COOH (the last two processes take place relatively readily), etc. It has been suggested[29] that the ease of elimination of the functional group Y from the molecule RY for the same R is inversely related to the proton affinity of the HY molecules and the following sequence, in terms of increasing ease of elimination of the most common functional groups, has been proposed (based on the proton affinities taken from Haney and Franklin[37]):

$$NH_2 < CH_3S \simeq C_6H_5 \simeq CH_3O \simeq OC(:O)H < CN \simeq SH < OH < I \simeq Cl \simeq Br\ .$$

The influence of the nature of R on the ease of elimination of the functional group can be estimated from general considerations. Thus, if R is an alkyl group, then the ease of elimination of Y increases in the sequence[38]: $k_{prim} < k_{sec} < k_{tert}$.

The substrate molecule is protonated only if the proton transfer from the reagent ion is an exothermic reaction. The heat of proton transfer is determined by the proton affinity of the substrate molecule M and that of the conjugate base X of the reagent ion, which is a measure of the acid properties of the reagent ion as a Brønsted acid: $\Delta H = PA(X) - PA(M)$. Consequently, by varying the acid strength of the reagent ion, it is possible to vary the exothermic property of the proton transfer reaction and hence the degree of fragmentation[23].

It can now be regarded as established that thermally activated fragmentation can occur under CI conditions. Thus the extremely significant influence of the temperature of the ion source on the degree of fragmentation of t-pentyl acetate and benzyl acetate in the presence of iso-C_4H_{20} has been noted[12]. It was found that CH_3COOH is eliminated with absorption of heat. Furthermore, when account was taken of the insignificant exothermic effect of protonation in the presence of iso-C_4H_{10} (between −8 and −13 kcal mole^{-1}) and the large number of collisions (approximately 200) of the protonated ion with the surrounding gas molecules, it could be claimed with sufficient confidence that the weakly excited ions formed initially rapidly reach thermal equilibrium with the surrounding medium, i.e. their distribution with respect to energies becomes of the Boltzmann type or approaches the latter. Kinetic analysis of experimental data obtained from iso-C_4H_{10} spectra recorded over a fairly wide temperature range showed that the rate constants for the unimolecular decomposition of ions obey the Arrhenius equation[12]. The use of reagent ions with fairly high acid strengths leads to fragmentation in a vibrationally excited state before the attainment of thermal equilibrium with the surrounding medium. For example, the protonated molecular ion of N-valeryl-leucine, formed in a methane plasma, decomposes in the energy state equivalent to the energy state of the same ion in the isobutane plasma at a temperature higher by 167 ± 10 K than the temperature of the methane plasma[39]. Thus, when the CIM-spectra obtained with different reagent gases are compared, the temperature of the ion source must be taken into account.

III. MASS SPECTRA OF THE CHEMICAL IONISATION OF DIFFERENT CLASSES OF ORGANIC COMPOUNDS

The most important factor in the study of the CI-fragmentation of organic compounds is that the reactions occurring in the ion source of the mass spectrometer obey the majority of the rules developed for ion–molecule reactions in the condensed phase. As one of the "mildest" ionisation methods, the CI procedure is most suitable in the study of the structures of labile molecules; it ensures

† As in the previous example, here the peak intensity is expressed as a percentage relative to the overall ionic current.

as a rule the presence of an intense peak due to the quasi-molecular ion for a fairly high degree of fragmentation. The nature of fragmentation in CI gives rise to the hope that this method will be most useful in the study of the content of functional groups in the substrate molecule and in the study of the nature and sequence of large blocks joined by labile bonds in the molecule. In ionisation by electrons [the electron impact (EI) method] the molecule is subjected to a more severe influence, as a result of which one can obtain data for the structure of its rigid skeleton. Thus the two methods (CI and EI) yield mutually supplementary information about the molecular structure.

1. Alkanes

The CH_4 spectra of n-alkanes consist of the peak due to the ion $[M - 1]^+$, which has the maximum intensity, and the peaks of the fragment alkyl ions, whose intensities are approximately equal but much lower than that of $[M - 1]^+$, located at intervals of 14 a.m.u.[8] The relative intensity of the ion $[M - 1]^+$ is independent of chain length, and the form of the CH_4 spectra, for example, for $n\text{-}C_{44}H_{90}$ and $n\text{-}C_8H_{18}$, is completely analogous. On the other hand, in the electron impact (EI) ultraviolet spectra of n-alkanes the maximum intensity corresponds to the $C_3H_7^+$, $C_4H_9^+$, and $C_5H_{11}^+$ ions, while the intensity of the peaks due to ions with large masses rapidly decreases with increase of m/e.[40] In the CH_4 spectra of branched alkanes the intensity of the ion $[M - 1]^+$ is somewhat lower than for n-alkanes, but the decrease is much smaller than in the case of electron impact, where the M^+ intensity becomes negligibly small[40]. The rate of dissociation of the C–C bond at the branching site increases appreciably, which can be attributed to exothermic β-cleavage (on the other hand, for unbranched alkanes the β-cleavage reaction is endothermic[8]):

$$CH_3CH_2CH_2\text{—}\overset{\curvearrowright}{CH_2}\text{—}\overset{+}{C}H\text{—}C_{13}H_{27} \longrightarrow CH_3CH_2CH_2^+ + C_{15}H_{30}\ ; \qquad (17)$$

(V) (endothermic process)

$$C_6H_{13}\text{—}\underset{C_3H_7}{\underset{|}{CH}}\text{—}\overset{\curvearrowright}{CH_2}\text{—}\overset{+}{C}HC_4H_9 \longrightarrow C_6H_{13}\text{—}\overset{+}{C}H\text{—}C_3H_7 + C_6H_{12}\ . \qquad (18)$$

(VI) (exothermic process)

In the CH_4 spectrum of compound (VI) the peaks of the fragment alkyl ions $C_{13}H_{27}^+$ and $C_{10}H_{21}^+$ are appreciably more intense compared with those of other alkyl ions. In addition, the olefin ions $C_{13}H_{26}^+$ and $C_{10}H_{20}^+$, which have a considerable diagnostic importance, are formed in small but detectable amounts; the mechanism of the formation of these ions has not been elucidated. Until recently, it has been suggested that the fragment alkyl ions are formed in n-alkanes exclusively as a result of the electrophilic attack by the reagent ion on the C–C bond[8]. It has now been demonstrated experimentally that their formation via an alternative mechanism with abstraction of an olefin from the ion $[M - 1]^+$ also takes place[41].

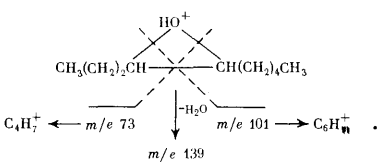
2. Cycloalkanes

Two series of ions have been detected in the CH_4 spectra of cycloalkanes: (1) $[M + 1]^+$ and $C_nH_{2n+1}^+$—the series of alkyl ions; (2) $[M - 1]^+$ and $C_nH_{2n-1}^+$—the series of alkenyl ions. The ion $[M + 1]^+$ is formed as a result of exothermic proton transfer from the reagent ion on ring opening. The ion $[M - 1]^+$ is formed when a hydride ion is split off from the cycloalkane molecule; it has the maximum intensity in the spectra. The study of the CH_4 spectra of cyclo-C_6D_{12} led to the conclusion that there is no hydrogen exchange between the substrate molecule and the reagent ions and that the $C_6D_{11}^+$ ion has the cyclohexyl and not the alkenyl structure. The presence of the $C_3D_7^+$ and $C_3D_6H^+$ ions indicates the occurrence of rearrangements with migration of hydrogen, because these ions originate from the hexyl ion $C_6D_{12}H^+$ and their peaks have approximately equal intensities[42].

3. Alkenes and Alkynes

The CH_4 spectra of monoalkenes resemble those of cycloalkanes, but the degree of fragmentation and the relative peak intensities corresponding to low m/e are greater for monoalkenes. Hydrogen is split off most readily from allyl positions. For polyenes, cycloalkenes, and alkynes, two series of ions are also observed, one of which originates from the quasi-molecular ion $[M + H]^+$ and the other from the quasi-molecular ion $[M - H]^+$.[43] A technique has been developed for the determination of the position of the double bond in the molecule of the initial olefin via its epoxy-derivative, using CH_4 or iso-C_4H_{10} as reagent gases (this method requires not more than 1 μg of the test substances):

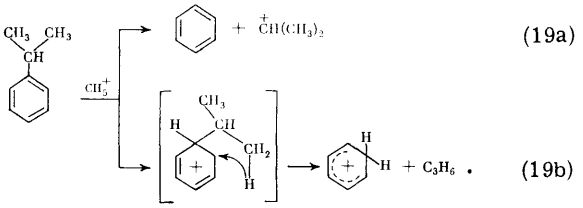
Scheme 1



The position of the epoxide ring and hence of the double bond can be readily established from the fragment peaks (see Scheme 1). Unfortunately no differences have been observed between the *cis*- and *trans*-isomers in any of the CIM-spectra of the epoxy-derivatives investigated[44].

4. Aromatic Hydrocarbons[45]

Aromatic rings are resistant to the action of reagent ions of the first type (see Table). For example, ions with a mass smaller than that of M^+ are not observed in the CH_4 spectrum of benzene. Together with the ions $[M + H]^+$, cluster ions having the composition $[C_6H_6 + C_2H_5]^+$, $[C_6H_6 + C_3H_5]^+$, etc. are formed. Alkyl groups are readily split off in the form of carbonium ions [reaction (19a)]. Furthermore, the alkyl side groups in aromatic hydrocarbons can undergo a fragmentation analogous to that of alkanes (see above). A hydride ion is split off from methyl groups with formation of a benzyl cation. In the presence of a side chain with three and more carbon atoms reactions involving hydrogen transfer and the elimination of an olefin [reaction (19b)] take place:



(19a)

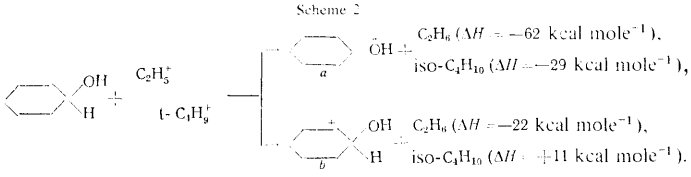
(19b)

5. Alcohols

The form of the iso-C_4H_{10} spectra of alkanols depends on the length and degree of branching of the hydrocarbon chain. For the first three members of the homologous series, the peak of the ion $[M + 1]^+$ has the maximum intensity in the spectrum. With increase of the length of the hydrocarbon chain, the intensity of the $[M + 1]^+$ peak falls sharply and the latter is altogether absent from the spectra of members of this series starting with C_8. The peak of the ion $[M - 1]^+$ is present with a fairly high intensity in the iso-C_4H_{10} spectra of all alcohols, with the exception of tertiary alcohols. The mechanisms of the formation of the ion $[M - 1]^+$ have been discussed in a number of studies[38,46,47]. One should note in the first place that initially the formation of this ion was considered exclusively in terms of hydride transfer from the alcohol molecule to the reagent ion[38]. However, the metastable transition $[M + 57]^+ \xrightarrow{*} [M - 1]^+$ has been observed[47]. Consequently at least some of the ions $[M - 1]^+$ should be formed when C_4H_{10} is split off from $[M + t\text{-}C_4H_9]^+$.

The initial hypothesis that α-hydrogen is split off preferentially in the spectra with CH_4 also proved to be invalid, because it was soon found[46] that in the CH_4 spectrum of 1-decan-1,1-d_2-ol the observed degree of elimination of α-deuterium would be expected on statistical grounds (10%). A more detailed study of this problem was undertaken[47] and it was found that specific elimination of α-deuterium is not observed in the CH_4 spectrum of cyclohexan-1-d-ol, but the extent of this process is inconsistent with that expected on statistical grounds. On the other hand, in the presence of iso-C_4H_{10} α-deuterium is split off preferentially (93%). It has been suggested that the abstraction of hydrogen is determined by the thermochemistry of competing reactions (Scheme 2):

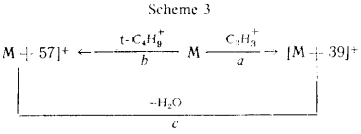
Scheme 2



If one takes into account the fact that endothermic reactions in CI are slow, it is not surprising that in the presence of iso-C_4H_{10} a specific exothermic reaction, involving the formation of the ion a with elimination of α-hydrogen, takes place, while in the presence of CH_4 the specific elimination of α-hydrogen is not observed (see Scheme 2).

The intensity of the peaks of the cluster ions observed in the iso-C_4H_{10} spectra of alcohols, namely $[M + 39]^+$, $[M + 57]^+$, and $[2M + 1]^+$, depends greatly on the conditions under which the spectrum is recorded[38]. Earlier studies of the CI-fragmentation of alcohols[38] led to the idea that the ions $[M + 39]^+$ and $[M + 57]^+$ are formed via pathways a and b:

Scheme 3



However, in spectra with a high resolution only the peaks of ions having the composition $[M + C_4H_9 - H_2O]^+$ were found and not $[M + C_3H_3]^+$.[47] Consequently the ion $[M + 39]^+$ is formed when H_2O is split off from $[M + 57]^+$ (pathway c). It has been observed recently that the initial reaction between t-$C_5H_{11}OH$ and iso-C_4H_{10} involves the formation of the cluster ion $[C_9H_{20}OH]^+$, which rapidly dissociates with formation of $[C_9H_{19}]^+ + H_2O$ and $[C_5H_{11}]^+ +$ neutral products[48]. It is noteworthy that in the iso-C_4H_{10} spectra of alkanols, starting with C_5, the C_nH_{2n+1} peak has the maximum intensity in the spectrum. When CH_4 is used, the ion decomposes further with formation of a series of alkyl and alkenyl ions[38].

As regards the analytical applications of CI, it is of interest to examine the method whereby primary, secondary, and tertiary alcohols can be distinguished, and which is based on the significant differences between the ease of elimination of the hydride ion from the molecules of these compounds. When $(CH_3)_2CO$ or CH_3CHO is added to CH_4 in proportions of 20 : 1, methane reagent ions react almost completely with the carbonyl compound [reaction (20)]:

$$CH_5^+ (C_2H_5^+) + (CH_3)_2CO \rightarrow CH_4 (C_2H_4) + [(CH_3)_2COH]^+, \quad (20)$$

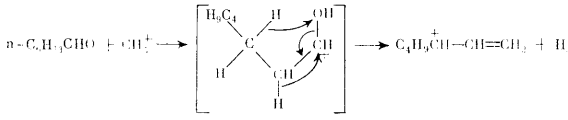


(21)

The oxonium ions formed in reaction (20) interact with secondary alcohols. This involves the elimination of hydrogen (in all probability from the α-position) and the formation of the ion $[M - 1]^+$ [reaction (21)]. An analogous reaction with primary alcohols takes place only in the presence of acetaldehyde. The ion $[M - 1]^+$ is not formed from tertiary alcohols[49].

6. Aldehydes and Ketones

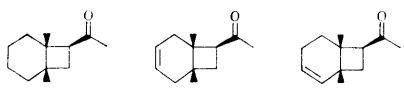
The CH_4 spectra of aliphatic aldehydes contain the peak due to the ion $[M + H - H_2O]^+$ in addition to that of the ion $[M + 1]^+$:



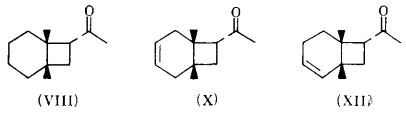
(22)

The driving force of reaction (22) is apparently the formation of a substituted allyl ion[50]. However, it must be emphasised that there is at present no independent evidence for the elimination of β-hydrogen from aldehyde molecules.

The CH_4 spectra of aliphatic ketones recorded under analogous conditions do not contain the $[M + H - H_2O]^+$ peak. Thus the spectrum of 2-octanone $C_{16}H_{13}COCH_3$ consists virtually of three peaks: $[M + 1]^+$, $[M + 29]^+$, and $[M + 41]^+$.[50] However, one should note that the formation of the ion $[M + H - H_2O]^+$ has been observed in the bicyclic ketones (VII)–(XII) and it has been found that the $[M + H - H_2O]^+$ peak for the *endo*-isomers (X) and (XII) is twelve times more intense than for the *exo*-isomers (IX) and (XI).[51] A test based on Dreiding models showed that the carbonyl oxygen in the *endo*-isomers (VIII), (X), and (XII) can approach closely to the hydrogen atoms of the six-membered ring, whereas in the *exo*-isomers it cannot. However, an increase of peak intensity is observed only for (X) and (XII) but not for (VIII), because in compounds (X) and (XII) hydrogen is transferred from the allyl position to the carbonyl group[51]:



(VIII) (IX) (XI)

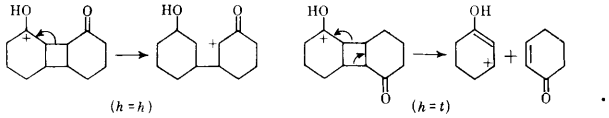


(VIII) (X) (XII)

7. Photodimers of Cyclic α,β-Unsaturated Ketones

The photodimerisation of α,β-unsaturated ketones results in the formation of isomeric compounds: $(h-h)$ and $(h-t)$. Comparison of the intensities of the peaks of the ions $[M+H]^+$ and $[M/2+H]^+$ in the CH_4 spectra of these compounds[52] showed that the intensity of the $[M/2+H]^+$ fragment peak for the $(h-h)$ isomers is appreciably lower than for the $(h-t)$ isomers. This fairly general phenomenon was explained by the fact that, in the β-cleavage of the C–C bond in the $(h-h)$ isomer, the positive charge must be localised in the vicinity of the carbonyl group, which inhibits the fragmentation[52]:

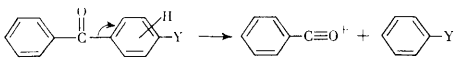
Scheme 4



$(h=h)$ $(h=t)$

8. Substituted Benzophenones[53]

The peaks of the ions $[M+H]^+$ and substituted and unsubstituted benzoyl ions were observed in the CIM-spectra of substituted benzophenones. It is believed that an increase of electron density at the substituted benzene ring leads to its preferential protonation. Since the fragmentation of the ion $[M+H]^+$ formed in this case leads to the formation of an unsubstituted benzoyl ion, its intensity in the CIM-spectrum increases:

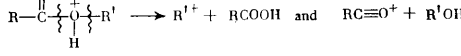


(23)

Protonation of the carbonyl oxygen apparently leads to the stable ion $Ar-\overset{+}{C}OH-Ar$, which exhibits no tendency towards fragmentation. Under electron impact, electron-donating substituents promote the formation of substituted benzoyl ions, probably in consequence of the stabilisation of the positive charge produced.

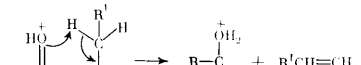
9. Esters

The peak of the ion $[M+H]^+$ in the CIM-spectra of esters is fairly intense (5% of the overall ionic current in the CH_4 spectrum of n-heptyl propionate) and exhibits no tendency towards a decrease with increase in the length of the hydrocarbon chain of the alcohol for a specified acid group. The ions R'^+ and $R-C\equiv O^+$, formed in heterolytic α-cleavage, give rise to moderately intense peaks:

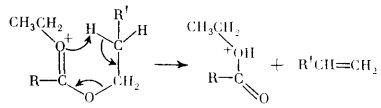


(24)

Alkenyl ions, formed when H_2 is split off from alkyl ions, are observed. As in the McLafferty rearrangement, processes responsible for β-cleavage lead either to the formation of the ion of a protonated carboxylic acid, which usually exhibits the maximum intensity in the spectrum [reaction (25)], or to transesterification if addition of the reagent ion takes place instead of protonation [reaction (26)]:



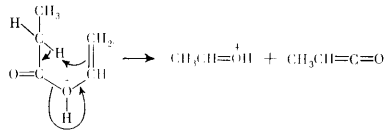
(25)



(26)

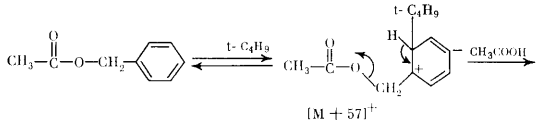
In the latter case ions with a moderate peak intensity are formed[54,55].

If the alcoholic component of the ester molecule possesses basic properties, for example, contains a double bond, it can itself serve as a proton acceptor. In this case reactions of type (25) and (26) are suppressed and are replaced by a proton transfer reaction with formation of a protonated aldehyde and the elimination of a keten-like molecule[54]:



(27)

The additional nucleophilic centre can also become an acceptor of the reagent ion[56]. This concept made it possible to identify the ions $[M-3]^+$ in the iso-C_4H_{10} spectra of acetates, which had not been previously assigned[56,57]:



(28)

For formates, these ions are manifested as $[M+11]^+$ species, for propionates as $[M-17]^+$ species, etc.

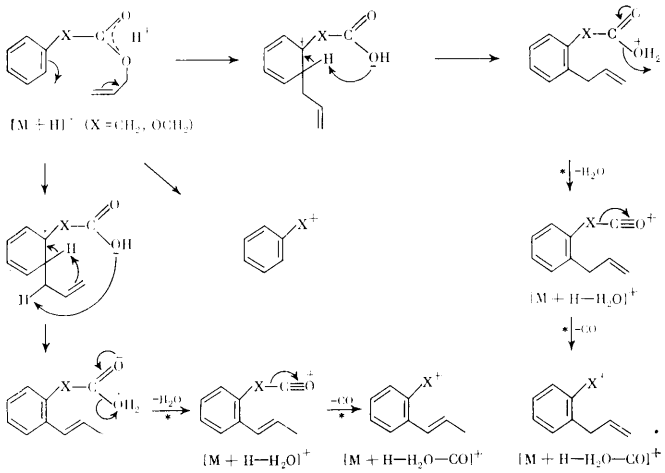
10. Fragmentation of Allyl Phenylacetates as an Example of Skeletal Rearrangements in Chemical Ionisation[58]

Under electron impact, the decomposition of the molecular ion is frequently accompanied by rearrangements[50,60]. In CI the rearrangements, particularly skeletal rearrangements, are encountered much more rarely. Field and Munson noted the occurrence of skeletal rearrangements in the bicyclo[2,2,2]octane[42], bicyclo[2,2,2]octene[43], and norbornadiene[61] systems using CH_4 as the reagent gas. The ions formed as a result of the rearrangements constitute approximately 18% of the overall ionic current. The formation of the rearranged ion $[CH_2OH]^+$ has been studied[62] in the protonation of $(CH_3)_2CO$ using H_2 as the reagent gas.

In the CH_4 spectra of allyl phenylacetate and allyl phenoxyacetate the ions formed in skeletal rearrangements constituted more than 40% of the overall ionic current[58]. The principal pathway to the fragmentation of the above compounds involves skeletal rearrangements and includes the successive elimination of elements of H_2O and CO from $[M+H]^+$ (Scheme 5). The *o*-allylation stage is analogous to the reaction in the condensed phase (the Claisen rearrangement)[63,64]. Allyl *ortho*-substitution is accompanied by the migration of H to the carbonyl group either from the *ortho*-position in the ring or from the allyl group. In

both cases the driving force of the reaction is the rearomatisation of the ring before the elimination of H_2O. If both *ortho*-positions in the ring are blocked, as, for example, in allyl 2′,6′-dichlorophenylacetate, then a simple ester fragmentation is observed, i.e. the splitting off of allyl alcohol with subsequent elimination of CO. Electron-accepting groups in the *para*-position also suppress *o*-allylation. Electron donors in the *para*-position promote a sharp intensification of competing fragmentation reactions with formation of benzyl (tropylium) ions. There is no rearrangement on ionisation by electrons and only the formation of tropylium ions is observed. Thus the EI-sprectra of allyl phenylacetates are simpler than the CIM-spectra.

Scheme 5



11. Amines

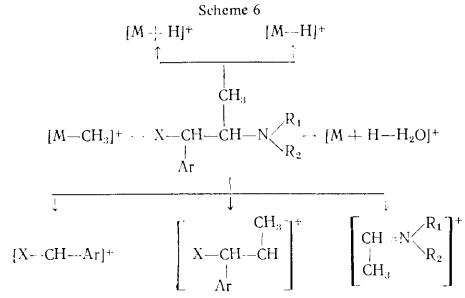
It has already been noted that the NH_2 group belongs to those which "leave with greatest difficulty" the protonated substrate molecule (Section II). Similarly the peak of the ion $[M + H]^+$ has the maximum intensity in the CIM-spectra of amines. The main fragmentation process on protonation of the amine molecule is due to the α-cleavage of the C–C bond relative to N. Thus the intensity of the peak with *m/e* 142 in the CH_4 spectrum of tributylamine is 19.9% of the overall ionic current, which is apparently due to the stabilising influence of the nitrogen atom[8,20]:

$$(n\text{-}C_4H_9)_3N + CH_5^+ \rightarrow \underset{m/e\ 142}{(n\text{-}C_4H_9)_2\overset{+}{N}{=}CH_2} + C_3H_8 + CH_4 \quad . \qquad (29)$$

The peak of the ion $[M - H]^+$ has a high intensity, probably for the same reason. Ions due to β- and γ-cleavage give rise to peaks with low and approximately equal intensities. The very intense peak due to the ion $[M - C_4H_9]^+$ was observed in the H_2 spectrum of tributylamine[65]. The postulate that the degree of fragmentation is independent of chain length, which is general for CI with transfer of even-electron species, has been confirmed in relation to polymeric tertiary amines[66].

The CH_4 spectra of four types of phenethylamine [α-amphetamine (XIII), *dl*-metamphetamine (XIV), *dl*-ephedrine (XV), and *dl*-methylephedrine (XVI)] have been investigated. There is no peak of the molecular ion in the EI-spectra of these compounds. The maximum peak of the ion $[CH_3{-}CH{=}N^{R_1}_{R_2}]^+$ is due to the α-cleavage of the C–C bond in relation to N and, with the exception of low-intensity ionic peaks with *m/e* 91 ($C_7H_7^+$) for (XIII) and *m/e* 77 ($C_6H_5^+$) for (XV), other characteristic peaks are absent from the EI-spectra of (XIII)–(XVI).

Scheme 6



(XIII): X = H, $R_1 = R_2 = H$;
(XIV): X = H, R_1 = H, $R_2 = CH_3$;
(XV): X = OH, R_1 = H, $R_2 = CH_3$;
(XVI): X = OH, $R_1 = R_2 = CH_3$.

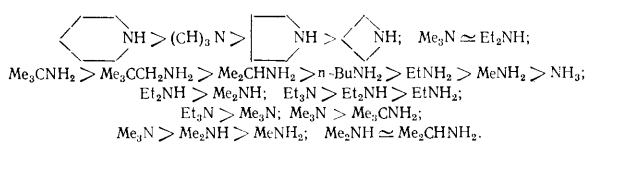
On the other hand, Scheme 6 shows that the CH_4 spectra of these compounds would alone be sufficient for the complete determination of their structure[65].

12. The Relative Basicity of Amines in the Gas Phase

The knowledge of relative basicities in the gas phase is of considerable interest for theoretical chemistry, since it makes it possible to infer the internal electronic effects in the molecule in the absence of a solvent. The determination of the relative basicities by the CI method is based on the fact that proton transfer is observed only in exothermic reactions with a negligible activation energy, i.e. the reaction

$$XH^+ + M \rightleftarrows X + MH^+ \qquad (30)$$

can proceed to the right only when $PA(M) > PA(X)$ (Section II). The relative basicities of amines determined in this way can be arranged in the following sequences[67]:



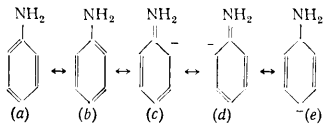
In conformity with the $+I$ effect, when the hydrogen in NH_3 is replaced by alkyl groups, the basicity of the amine should increase, which we observed in the gas phase. However, in solution there is a different order of basicities owing to the influence of solvation. For example, in aqueous solutions the basicity of methylamines falls in the following sequence:

$$Me_2NH > Me_3N > MeNH_2 > NH_3.$$

The explanation of this phenomenon is that the stabilisation of the system as a result of the formation of hydrogen bonds with H_2O diminishes with decrease of the number of H atoms linked to N and in the case of Me_3N the given effect predominates over the increase of the stability of the cation due to the $+I$ effect of the methyl groups[67,68].

In aqueous solutions the basicity of anilines is much lower than that of ammonia and methylamines [$pK_b(C_6H_5NH_2) = 9.42$; $pK_b(NH_3) = 4.77$]. An attempt was made to account for this finding by the contribution of resonance structures (*c*)–(*e*) to the additional stabilisation of anilines, which

would vanish on protonation, and also by the electron-withdrawing influence of the phenyl group[69]:



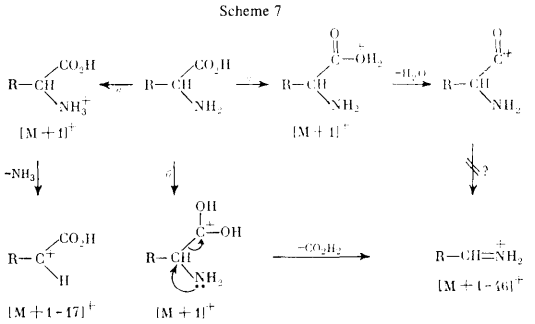
However, the difference between the resonance energies of benzene and aniline is not more than 2–4 kcal mole^{-1} and the contribution of structures (*c*)–(*e*) to the resonance stabilisation should be minimal, since they include charge separation. In the gas phase aniline is more basic than NH_3, which can apparently be accounted for by the high polarisability of the phenyl group, stabilising the positive charge. This hypothesis is confirmed by the fact that the basicity of *N*,*N*,*N*-triphenylamine is higher than that of aniline[70].

The low basicity of pyridine (lower than that of NH_3) has nowadays come to be explained by the sp^2 hybridisation of the N-atom, but, it has been shown[70] that in reality the basicity of pyridine in the gas phase exceeds that of dimethylamine and that the reason for the low basicity of pyridine in aqueous solution should therefore be sought in the first place in the effect of solvation and not hybridisation.

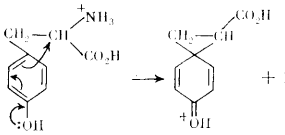
13. Aminoacids and Peptides

The presence of the ions $[M + 1]^+$, $[M + 1 - 18]^+$, $[M + 1 - 17]^+$, and $[M + 1 - 46]^+$ is characteristic of the CIM-spectra of the majority of aminoacids[71,72]:

Scheme 7

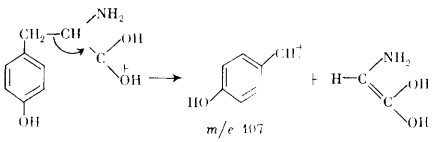


The fragmentation of glutamic acid, arginine, citrulline, and ornithine does not fit within the framework of this scheme[73]. The ion $[M + 1]^+$ has high-intensity peaks in all cases; the above aminoacids, where the peak due to the ion $[M + 1 - 18]^+$ has a high intensity and which are formed on pyrolytic elimination of H_2O, are an exception. The fragmentation of glycine, alanine, valine, leucine, isoleucine, and proline is confined to pathways *a* and *b*. A second H_2O molecule is abstracted from hydroxyaminoacids—serine, threonine, and 3-hydroxyproline. The peak due to the metastable ion, confirming the abstraction of CO, has not been observed in any of the CIM-spectra of aminoacids[72]. Fragmentation with elimination of elements of CO, which is extremely common under electron impact, is apparently encountered very rarely under CI conditions. The abstraction of NH_3 from $[M + 1]^+$ is of greatest theoretical interest. The fact that the peak of the ion $[M + 1 - 17]^+$ is not observed in the spectra of unsubstituted aliphatic aminoacids is evidence against a simple interpretation of the elimination, represented in Scheme 7 (pathway *b*). The elimination of elements of NH_3 is observed only for aminoacids containing a second nucleophilic group, which apparently indicates the involvement of this group in substitution and is accompanied by the formation of new bonds, for example:



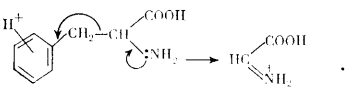
(31)

Such "co-operative" reactions are apparently of general importance in CI-fragmentation processes involving molecules of compounds with two and more nucleophilic centres (see, for example, Chizhov et al.[95]). The fairly intense peak of the ion with *m*/*e* 107, formed on cleavage of the α,β-bond, merits attention in the CIM-spectrum of tyrosine:



(32)

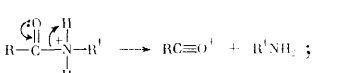
An analogous cleavage has been observed also for other aromatic aminoacids: phenylalanine, tryptophan, and histidine. In the absence of electron-donating substituents, the charge can be localised also on the amino-fragment:



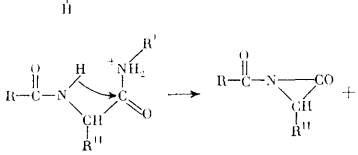
(33)

One of the most important methodological problems in bio-organic chemistry at the present time is the determination of the aminoacid sequence in peptides. The solution of this problem by mass spectrometry is based on the preferential cleavage of amide bonds in the ionisation of the peptide molecule[74]. To ensure their adequate volatility, peptides are modified by acylating the terminal amino-group and esterifying the terminal acid group. The EI-spectra usually contain only a complete set of amino-fragments (acylium ions). In addition, the interpretation of the EI-spectra of peptides is complicated as a result of the fragmentation of the molecules with elimination of side chains and requires the use of high-resolution mass spectrometers. The low peak intensities in the region of high masses lower the sensitivity of the method.

In CI there is usually a complete set of fragments of both the amino-type [reaction (34)] and the acyl type [reaction (35)]:



(34)



(35)

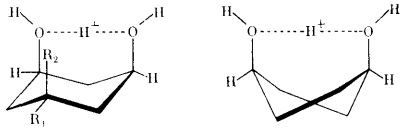
The presence of two series of ionic peaks in the CIM-spectra of peptides reduces the uncertainty in the determination of the aminoacid sequence and one can use for this purpose mass spectra with single focussing[75]. Owing to the lower degree of fragmentation and the relatively small difference between the densities of peaks due to ions with large and small masses, a much smaller amount of the specimen is required than in the recording of the EI spectrum (by a factor of approximately 100).[76] The CI method makes it

possible to record the spectra of peptides with a higher molecular weight than in the EI method.

The determination of satisfactory mass spectra of involatile substances and particularly peptides is one of the fundamental and most difficult problems in modern mass spectrometry. The most promising approaches in this field are those which do not require the modification of the initial substance in order to increase its volatility. Thus the application of the desorption method in an electric field apparently makes it possible to investigate unmodified peptides with a lower volatility and a greater variety of aminoacids than in the CI method[77]. However, the number of fragment ion peaks in the mass spectrum is frequently insufficient for the determination of the aminoacid sequence in the initial peptide. Considerable advances have been made recently also in the determination of the CIM-spectra of involatile substances by means of special methods[78-80]. Satisfactory spectra have been obtained for nonapeptides containing unprotected arginine and histidine, which made it possible to determine unambiguously the aminoacid sequences[78].

14. The Dependence of the Fragmentation in CI on the Stereochemistry and Conformation of Molecules in Relation to Cyclic Polyols and Steroid Aminoalcohols

As early as 1971, it was established[46] in relation to α,ω-diols, α,ω-dithiols, and α,ω-diamines with a long hydrocarbon chain that the formation of intramolecular hydrogen bonds stabilises the quasi-molecular ion $[M+H]^+$.[46] This phenomenon was used to investigate the stereochemistry of cyclic polyols[81]. The formation of proton bridges in the chair-conformation of *cis*-cyclohexane-1,3-diol (XVII) or the twist-form of *cis*-cyclohexane-1,4-diol (XVIII) lead to a marked suppression of the elimination of H_2O molecules from $[M + H]^+$. The addition of a third hydroxy-group to the molecule to give (XIX, R_2 = OH) results in a further stabilisation of the ion $[M + H]^+$ in consequence of the formation of two additional hydrogen bonds.



(XVII)

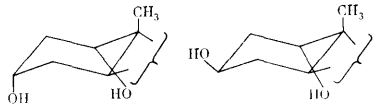
(XVIII)

(XVII): $R_1 = R_2 = H$;
(XIX): $R_1 = H$, $R_2 = OH$;
(XX): $R_1 = H$, $R_2 = CH_3$.

The presence of a bulky substituent in the 5-position in (XX, $R_2 = CH_3$) destabilises the structure with a proton bridge and increases the degree of fragmentation. It is noteworthy that this increase is more pronounced for a high ionisation energy (CH_4 or iso-C_4H_{10} at high temperatures).

In contrast to their *cis*-isomers, the CIM-spectra of *trans*-cyclohexane-1,3-diol and *trans*-cyclohexane-1,4-diol contain intense peaks due to the ions $[M + H - H_2O]^+$ and $[M + H - 2H_2O]^+$, because stabilising proton bridges are not formed in the ions $[M + H]^+$ derived from these compounds. As in the spectra of monohydric alcohols, the spectra of the *trans*-isomers also contain an extremely intense peak due to the quasi-molecular ion $[M + H]^+$. It is believed[82] that a linear structure of the O...H⁺...O fragment, which cannot occur in *cis*- and *trans*-cyclohexane-1,2-diols, is necessary for the formation of a strong hydrogen bond; the flexibility of the cyclohexane ring leads to the final disappearance of the stereochemical advantage of the formation of the proton bridge in the *cis*-isomer, so that the CIM-spectra of *cis*- and *trans*-cyclohexane-1,2-diols are completely similar. However, the ion $[M + H]^+$ derived from cyclopentane-1,2-diols is appreciably more stable for the *cis*-isomer, which is probably associated with rigidity of the cyclopentane ring.

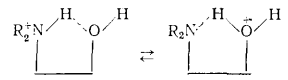
The results described above can be extended with reasonable confidence to more complex systems, although a significant difference between the stabilities of the ions $[M + H]^+$ derived from 5α-androstane-1α,3α-diol (XXI) and 5α-androstane-1α,3β-diol (XXII) was not observed[83].



(XXI) (XXII)

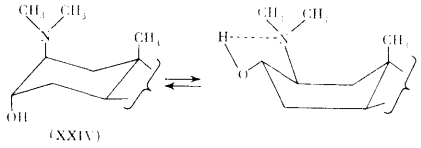
However, the use of milder ionisation conditions (95°C, direct injection of the specimen into the isobutane plasma[79]) made it possible to discover the differences between the spectra of (XXI) and (XXII) corresponding to the CIM-spectroscopic data for cyclohexane-1,3-diols[31].

When one of the hydroxy-groups is replaced by an amino-group, the main factor stabilising the quasi-molecular ion $[M + H]^+$ becomes proton transfer from oxygen to nitrogen in the bridge structure[83]:



(36)

This is why the *cis*-1,2- and *cis*-1,3-isomers are more stable than their *trans*-analogues, in which there is no proton transfer. It has been suggested[83] that the molecular conformation can play a very significant role in CI-fragmentation. The iso-C_4H_{10} spectra of 3α-dimethylamino-2β-hydroxypregnane (XXIII) and 2β-dimethylamino-3α-hydroxypregnane (XXIV) were interpreted from this standpoint. It has been shown by infrared spectroscopy[84] that an intramolecular hydrogen bond is formed in the corresponding *trans*-isomers of the cholestane series (evidently when the A ring of the steroid skeleton assumes the boat conformation):



(XXIV)

(37)

i.r.	30%	70%
CI	26.5%	73.5%

Using model compounds for which a transition to the boat conformation is known not to occur, the authors[83] estimated the conformational equilibrium for (XXIII) and (XXIV) on the basis of their iso-C_4H_{10} spectra. The results proved to be in excellent agreement with infrared spectroscopic data, which is extremely surprising bearing in mind the differences between the experimental conditions. Evidently further studies on these lines are extremely promising.

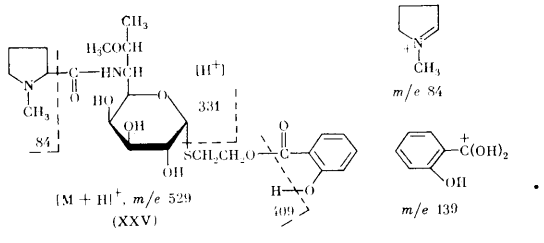
15. Carbohydrates, Nucleosides, and Macrolide Antibiotics

Mass spectrometry with electron impact is used nowadays to investigate carbohydrates and their derivatives[85]. When very small amounts of the specimen are available (sometimes $<10^{-6}$ g), valuable information about the molecular weight of the carbohydrate molecule, the nature and sequence of monosaccharide units, and in certain cases the position of the glycosidic linkages between the individual units can be obtained. The most suitable volatile derivatives for the study of the structures of oligosaccharides by the EI method are their acetates and methyl and trimethylsilyl ethers. However, the extremely low intensity and in certain cases the absence of the peak due to the molecular ion and the low intensities of the peaks due to fragment ions with high molecular weights impose very significant limitations on the analysis.

The most promising approach used to overcome these limitations involves the application of "mild" ionisation methods, for example, ionisation in a field[86], desorption in a field[86], and CI. It has been found that the degree of fragmentation under the conditions of ionisation in a field and desorption in a field is insufficient for the investigation of the structure. In studies involving the CI- fragmentation of carbohydrates and related compounds, the spectra of pentoses, hexoses, and their simple derivatives[32,87-92], oligosaccharide acetate[93,94], the methyl ethers of glycosyl- and biosyl-polyols[95], the antibiotics celesticetin and clindamycin, aminoacylthioglycosides[96,97], nucleosides[28,98,99], and macrolide antibiotics[24,100,101] were examined.

The results obtained fit within the framework of the generalisations developed in the study of the CIM-spectra of other classes of organic compounds. Thus the peak of the adduct ion $[M + NH_4]^+$ has been observed in the NH_3 spectra of oligosaccharide acetates (up to tetrasaccharides inclusive). The formation of this ion in the case of higher oligosaccharide acetates is apparently prevented by the thermal instability of these compounds when they are vaporised[93,94]. However, when the molecule contains a highly basic nitrogen atom, the peak of the ion $[M + NH_4]^+$ is absent from the NH_3 spectrum, since, instead of simple association, there is proton transfer from NH_4^+ to the nitrogen in the substrate molecule with formation of the ion $[M + H]^+$.[32] Thus the iso-C_4H_{10} and NH_3 spectra of the antibiotic celesticetin (XXV) differ markedly, because protonation in the presence of NH_3 can occur exclusively at nitrogen atoms remote from the aromatic part of the molecule and the formation of the ion with m/e 139 is strongly suppressed. On the other hand, in the iso-C_4H_{10} spectrum the ion has the maximum intensity, because protonation proceeds readily at the oxygen atom at the ester group of the salicylate. The peak of the methylpyrrolidinium cation with m/e 84 in the iso-C_4H_{10} spectrum has an extremely low intensity, while in the NH_3 spectrum its intensity is high[96]:

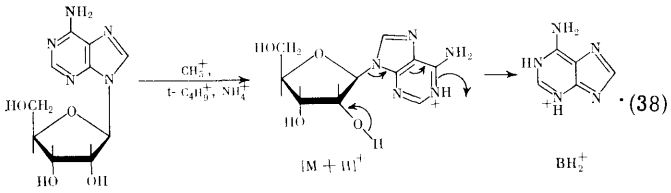
Scheme 8



The fragmentation of derivatives of pentoses and hexoses is extremely simple and in essence consists in successive and/or simultaneous elimination of functional groups, the degree of fragmentation being determined, as usual, by the acid strength of the reagent ions. For example, a detailed study of the fragmentation pathways of β-methyl-2,3,4,6-tetra-O-methyl-D-galactopyranoside using its deuterated analogues showed that the dominant process in the formation of ions with m/e 187 and 155 is the abstraction of methoxy-groups (in the form of methanol molecules) from the 3- and 4-positions and in the formation of ions with m/e 187 the most preferred process is abstraction from the 3-position. The first stage in the decomposition of the quasi-molecular ion $[M + H]^+$ with abstraction of methanol from the glycosidic centre was regarded as analogous to the rate-limiting stage in the acid hydrolysis of methylglycosides[90]. It has been shown[91] that the anomeric effect has a significant influence on the rate of decomposition of quasi-molecular ions and on the ratio of the intensities of the peaks due to the ions $[M+H]^+$ and $[M + H - CH_3OH]^+$ (m/e 251 and 219 respectively) and in the spectra of α- and β-methyl-2,3,4,6-tetra-O-methyl-D-galactopyranosides.

Examination of the iso-C_4H_{10} spectra of the methyl ethers of methyl deoxyhexosides led to the conclusion that the position of the deoxy-unit in 2,3-, 4-, and 6-deoxysaccharides can be determined from the ratio of the intensities of the peaks with m/e 125, 157, and 189 in spectra recorded at the same temperature[92].

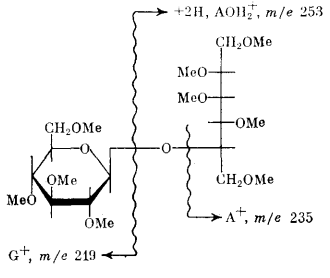
A complex aglycone, particularly when it contains powerful nucleophilic centres, tends to be split off in the form of a protonated species[27,88]. This decomposition pathway predominates in the CI-fragmentation of nucleosides:



(38)

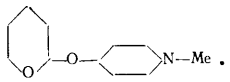
The formation of glycosyl ions in the given instance constitutes a much less probable fragmentation pathway[27,98]. The decomposition of the methyl ethers of glycosyl- and biosyl-polyols also proceeds with the preferential formation of the protonated aglycone (in this case the initial protonation apparently involves one of the five oxygen atoms in the methoxy-groups of the aglycone); however, also formed are the ions A^+ (probably on dissociation of the C–O bond on the side of the aglycone) and the glycosyl ion G^+ (with a much lower intensity) and it has been shown that the ratio of the intensities of the A^+ and AOH_2^+ peaks depends greatly on the position of the glycosidic linkage (1 → 2, 1 → 3, 1 → 4, and 1 → 6) in glycosylsorbitols[95]:

Scheme 9



The fragment ion peaks make it possible to determine directly the nature and sequence of the monomeric units of both glycosyl- and biosyl-polyols[95]. This is also true of the CIM-spectra of oligosaccharide acetates[93,94].

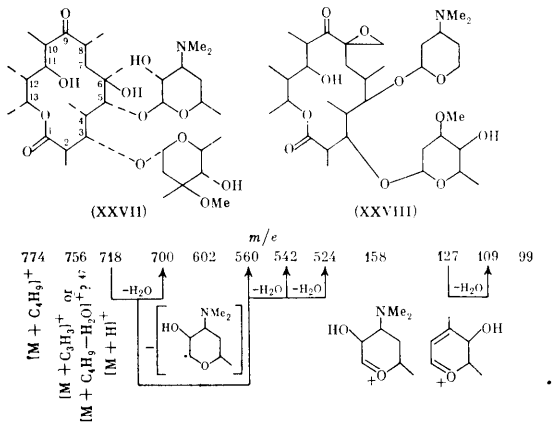
The ideas about the mechanism with the excitation centre remote from the site of bond dissociation were first formulated in the discussion of the fragmentation of macrolide antibiotics[100]. The possibility of fragmentation via this mechanism has been demonstrated rigorously and experimentally for compound (XXVI), which serves as a model of a glycoside with a complex aglycone[33]:



(XXVI)

The study of the CIM-spectra of macrolide antibiotics was stimulated by the fact that the EI peak of the molecular ion M^+ has an extremely low intensity and cannot always be detected. All the high-intensity peaks are located in the region of low mass numbers and the majority of them correspond to aminosugar fragments. The fragment ions corresponding to portions of the macrolide ring and neutral sugars are suppressed, so that it is extremely difficult to obtain structural information about these components of the molecule. On the other hand, in the iso-C_4H_{10} spectra of these compounds the peak of the ion $[M + H]^+$ has a very high intensity. The fragment ions in the middle part of the spectrum correspond to the successive elimination of sugar residues from $[M + H]^+$. Ions with low masses arise from sugar fragments when glyosidic linkages are broken with subsequent loss of one and more oxygen substituents—see Scheme 10 for the decomposition of the ion $[M + H]^+$ derived from erythromycin B (XXVII):

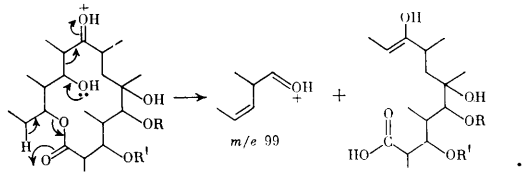
Scheme 10



(XXVII) (XXVIII)

Only the formation of fragment ions with *m/e* 99 and 602, giving rise to intense peaks, requires the dissociation of the C–C bond in the macrolide ring. The formation of an ion with *m/e* 99 can be regarded as the result of the protonation at the 9-oxo-group with subsequent opening of the ring at the lactone linkage as a result of the McLafferty rearrangement and the cleavage of the $C_{(10)}$–$C_{(11)}$ bond via a retroaldol type of fragmentation process (Scheme 11). The ion with *m/e* 602 corresponds to the protonated fragment (XXIX) after the elimination of one water molecule.

Scheme 11



(XXIX)

The structure of oleandomycin (XXVIII) resembles that of erythromycin B, but there are distinctive differences, the majority of which are clearly seen from the inspection of the iso-C_4H_{10} spectrum. Thus the peak of the ion arising in the retroaldol cleavage is very intense, but is displaced towards *m/e* 85, since the 13-substituent in (XXVIII) is a methyl group and not an ethyl group as in (XXVII). There is no peak due to the ion $[M + H - H_2O]^+$ in the spectrum of (XXVIII). This ion arises in acid-catalysed reactions involving macrolides which have a hydroxy-group in the 6-position, which is conformationally suitable for attack by the carbonyl group in the 9-position[102].

Information about the nature of the sugar units can be obtained by examining the ions arising in the cleavage of glycosidic linkages[24,100,101]. The iso-C_4H_{10} spectra of macrolide antibiotics with 16-membered rings have been examined[101]. They contain an extremely intense peak due to the $[M + H]^+$ ion and the peaks of fragment ions corresponding to the successive elimination of sugars and other smaller molecules—water, acetic acid, and methanol. The cleavage of C–C bonds is not a characteristic feature of the 16-membered macrolide ring.

The combination of CI, infrared, ultraviolet, and NMR spectroscopic methods and the mass-spectrometric method with electron impact together with a few rationally selected degradation reactions ensures a rapid and reliable determination of the structures of new compounds in this and related series.

IV. MASS SPECTROMETRY OF NEGATIVE IONS WITH CHEMICAL IONISATION. THE S_N2 REACTION IN THE GAS PHASE

Chemical ionisation by anions is significantly "milder" than ionisation by cations, which is understandable when one compares the proton (150–250 kcal $mole^{-1}$) and anion (5–25 kcal $mole^{-1}$)[17] affinities of molecules. Yet another cause of the "mildness" of CI by negative ions is associated with the fact that in the gas phase an odd-electron anion has sufficient energy for autoneutralisation, i.e. for the ejection of an electron, and the activation energy for the reaction must be very much smaller than the electron affinity of the neutral molecule. In the association of the molecule with an even-electron anion in the presence of an excess of internal energy there is a possibility of the reverse decomposition into a neutral species and an anion[17]. The CI-mass-spectrometry of negative ions has become readily available after the development of an ion source with a Townsend discharge, which makes it possible to obtain beams of positive and negative ions of comparable intensity[103,104]. The range of its analytical applications is limited apparently by the need to determine traces of substances, especially halogen-containing compounds (in particular, chlorine-containing pesticides[105] and insecticides[106]). Its application in general structural analysis is probably limited by inadequate fragmentation (however, see Hunt et al.[104]).

An interesting application of gas-phase reactions of anions as a guide to carrying out the corresponding reactions in solutions has been outlined[107].

The most fruitful application of the CI-mass-spectrometry of negative ions was found in physicochemical research. Having examined the changes in the heats and entropies of association of Cl^- in the series CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 and having taken into account the fact that 1-bromoadamantane and 1-bromo[2,2,2]bicyclooctane do not combine with Cl^-, Br^-, and I^-, Dougherty and coworkers concluded that the ionic clusters RXY^- (where X and Y are halogens) are identical with the S_N2 transition state in Finkelstein's reactions[14]. Thus the data obtained for these ions can be used to estimate the influence of the solvent on the reactivity in S_N2 reactions. Both the influence of the nucleophilic properties of the attacking base[15] and the structural influence of the alkyl groups[16] have been examined. It has been found that the nucleophilic properties of Cl^-, Br^-, and I^- in the gas phase are approximately the same and that the differences between the nucleophilic properties of the same bases in Finkelstein's substitution reactions are caused mainly by the changes in the relative degrees of solvation of the reactants and the transition states in exchange processes[15].

It is believed that a branched hydrocarbon group interferes with S_N2 reactions. Thus the exchange of the halogen in neopentyl bromide via an S_N2 mechanism is to a large extent suppressed[108]. However, this classical model is apparently applicable solely to S_N2 reactions in the condensed phase, because it has been found[16] that the heats of association of Br^- increase in the sequence MeBr < EtBr < iso-PrBr < t-BuBr (α-branching) and EtBr < iso-BuBr < neopentyl bromide (β-branching). The entropies of association of these compounds in the gas phase vary approximately in parallel with the corresponding changes in solution. The conclusion that the structural influences of the alkyl groups on the reactivity in S_N2 reactions in solution are controlled exclusively by solvation is therefore valid.

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The foregoing review shows that the CI method has been finding increasingly wide applications in the identification and determination of the structures of organic compounds. Its advantages when used for these purposes compared with the electron impact method consist in the presence of stable MH^+ ions even in those cases where the M^+ ion is unstable. This makes it possible to find the molecular weight directly from the CIM-spectra. The differences between the CIM-spectra of structural isomers and stereoisomers are frequently greater than in the EI method, which makes the CI method particularly valuable for the solution of structural and stereochemical problems, which cannot be solved by EI-mass-spectrometry. Furthermore, the CI method has proved extremely promising for the investigation of the mechanisms of various gas-phase reactions and the determination of the intrinsic values of fundamental characteristics of molecules and other species, such as basicity and nucleophilicity. All these factors give rise to the hope that new valuable results will be obtained in the immediate future with the aid of the CI method.

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Dinuclear and Polynuclear Complexes with Azomethine Ligands and Their Magnetic Properties

V.A.Kogan, V.V.Zelentsov, O.A.Osipov, and A.S.Burlov

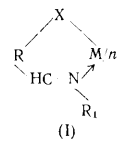
The review deals with di- and poly-nuclear metal complexes of Schiff bases whose magnetic properties are interpreted, within the framework of the exchange mechanism, as due to an exchange interaction between paramagnetic centres. The principal types of di- and poly-nuclear complexes with azomethine ligands and the factors influencing the strength and nature of the exchange interaction (the nature of the bridge groups and the stereochemistry of the coordination units) are examined. The problems of the specific selection of ligands for the synthesis of the above complexes are discussed.
The bibliography includes 112 references.

CONTENTS

I. Introduction 645
II. Complexes with tridentate and similar ligands 645
III. Di- and poly-nuclear complexes based on chelates with Schiff bases as ligands 648
IV. Dinuclear complexes with polydentate dimerising ligands 652

I. INTRODUCTION

Metal complexes of type (I) with azomethine ligands (Schiff bases) have been vigorously investigated since the 1930s.[1]



(I)

The experimental data accumulated hitherto[2-4] make it possible to deduce definite correlations between the electronic and molecular structures of these compounds, on the one hand, and their physicochemical properties, on the other. A detailed study of the structure–property relation is possible if one can vary (a) the ligand fragments R and R_1 in (I) while keeping constant the immediate environment of the metal atom, (b) the electron-donating atoms X (O, N, S, or Se) for the same R and R_1, and (c) the central atom M while keeping constant R, R_1, and X. Comparison of systematic series of complexes with a regular variation of particular physicochemical properties makes it possible to discover which structural factors are responsible for these changes[5,6].

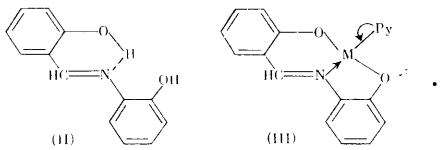
The wide variety of types of monomeric chelates becomes appreciably greater when di- and poly-nuclear compounds are formed from tri- and poly-dentate azomethine ligands or inner complexes of type (I). Compounds in which exchange interactions between paramagnetic centres are manifested are of greatest interest.

The use of azomethine compounds as ligands in order to obtain the so-called exchange-bound clusters makes it possible to follow the influence of stereochemical and electronic factors on the extent and nature of exchange interactions when substituents in the ligands and the ligands themselves are varied. The exchange properties of the complexes are determined by the structure of the ligand and the nature of the bridge groups.

This review deals with studies which illustrate most fully these characteristic features of di- and poly-nuclear complexes with azomethine ligands. The principal types of di- and polynuclear complexes with exchange interactions and factors which determine the specific selection of ligands in order to obtain these compounds are considered.

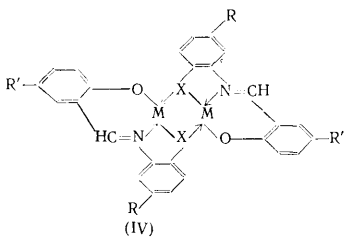
II. COMPLEXES WITH TRIDENTATE AND SIMILAR LIGANDS

The ability to form dimeric and polymeric complexes is always manifested when organic compounds with an appropriate structure, giving rise on interaction with the metal to coordination-unsaturated complexes in the monomeric state, are used. One of the most common types of compounds of this kind are complexes of 3*d* metals obtained on the basis of salicylidene-*o*-aminophenol (II):

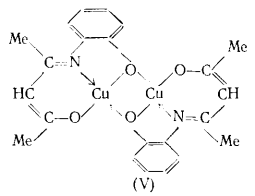


(II) (III)

If monomeric complexes (III) are formed, in which the fourth coordination site is occupied by a solvent molecule [in the present case pyridine (Py)], then they have effective magnetic moments μ_{eff} corresponding to a single unpaired electron (for example, with $M=Cu^{II}$).[7-9] If the monomers are coordination saturated by interaction with one another, dimeric complexes of types IV and V are formed:



(IV)



(V)

Here two paramagnetic centres are fairly close to one another and exchange interaction takes place between them. This was established for the first time for complexes of type (IV) (with M = Cu and X = O, [7-9] with M = VO and X = O, [10,11] and with M = Ni [12]) on the basis of the decrease of μeff relative to the "spin only" value. An analogous phenomenon was observed for complexes of type (V). [7,11-14] An X-ray diffraction study confirmed the dimeric structure of (V) in which the Cu–Cu distance is 2.99 Å, the temperature dependence of the magnetic measurement indicating the antiferromagnetic nature of this exchange interaction[13,14]. Cu^{II} and VO^{II} complexes of types (V) [11,17] and (IV) [15-22] with various substituents have been investigated particularly thoroughly[23]. Careful analysis of the temperature dependence of the magnetic susceptibilities of complexes of type (V) (μeff = 1.39–1.00 μB at 203–88 K) showed that it does not obey the Bleany–Bowers equation[24]†

$$\chi = \frac{Ng^2\beta^2}{3kT}[1 + 1/3\exp(2J/kT)]^{-1} + N\alpha, \qquad (1)$$

which takes into account only the exchange interaction between the paramagnetic ions in the dimeric molecule[17]. An additional interaction of the dimeric fragments with one another has been established for this compound as well as a number of other Cu^{II} and VO^{II} complexes of type (IV). [22,25]

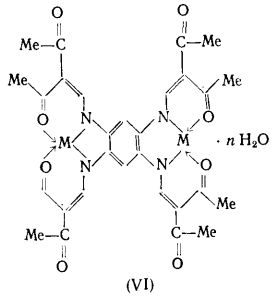
The study of complexes of types (IV) and (V) showed that the model taking into account only the direct metal–metal interaction, as a result of the partial overlap of the *d* orbitals of the metal atoms, cannot adequately account for the paramagnetism; ideas postulating an indirect exchange interaction via bridge groups X have been developed[10,11,14-17]. This was convincingly confirmed also by studies of the influence of the substituents R and R′ in (IV, N = Cu, X = O) on the strength of the exchange interaction in the dimeric molecules (Table 1)[15].

Table 1. The effective magnetic moments, *g*-factors, and exchange integrals for complexes of type (IV, M = Cu, X = O).

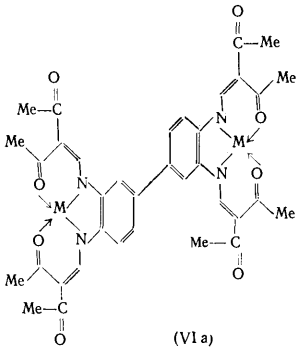
R	R′	*T*, K	μ_{eff}, μ_B	*g*	$-2J$, cm^{-1}
H	H	45—292	0.10—1.31	1.97±0.1	289±10
H	Me	47—296	0.11—1.47	2.10±0.1	245±10
H	Cl	43.2—296	0.15—1.25	2.16±0.1	371±25
H	Br	40—300	0.11—1.28	2.13±0.1	341±20
H	NO_2	20.7—294	0.17—1.25	—	—
Cl	H	4.95—295	0.10—1.60	1.86±0.1	46±20
NO_2	H	35—294	0.30—1.55	1.97±0.1	125±5
Cl	Cl	6.3—299	0.22—1.60	1.88±0.1	39±20
NO_2	NO_2	47—295	0.10—1.30	2.05±0.1	307±10

It has been shown that electron-accepting groups in the R′ position tend to increase the extent of the antiferromagnetic interaction, while the same groups in the R position tend to decrease it. From the standpoint of the mechanism[26] postulating that the indirect exchange is determined by the antibonding *d* orbitals of the metal and the hybrid *sp* orbitals of the ligand atoms, the different effects of the substituents R and R′ can be explained by the fact that electron-accepting substituents in the R′ position influence the non-bridging oxygen and nitrogen atoms, while those in the R position influence the bridging oxygen atom.

The use of complexes with azomethine ligands as models made it possible subsequently to obtain unambiguous evidence showing that the exchange interaction can be only indirect. Thus the magnetic properties of complexes (VI) and (VIa) were compared[27]:



(VI)



(VIa)

M=Cu^{II}, Ni^{II}, or VO^{II}.

A direct copper–copper exchange is ruled out in complex (VI), but, despite this, an antiferromagnetic interaction is observed between the copper ions with $2J = 12.2$ cm^{-1} (μeff = 1.8–0.42 μB at 216–4.2 K). It was assumed that the interaction is due to the polarisation of the spins of the unpaired electron of the copper atom and the electrons of the nitrogen atom, which is then distributed via the π-electron system of the benzene ring to the second copper atom. The presence of the C–C single bond in complex (VIa) prevents such delocalisation and an antiferromagnetic interaction is not observed (μeff = 1.83–1.69 μB at 241–4.2 K). [27]

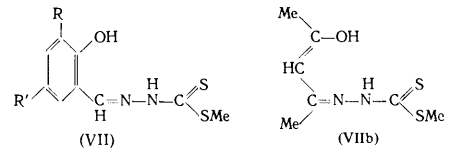
Sulphur-containing ligands also form di- and polynuclear complexes with exchange interaction[17,28,29]. As for complex (III), the addition of a pyridine molecule in these compounds promotes the formation of a complex with a normal magnetic moment[29]. When the bridging O atom is replaced by S, the magnetic properties of the complexes change.

The effective magnetic moments of complexes of type (IV, X = S, M = Cu) are almost independent of temperature (μeff = 1.73–1.85 μB at 291–80 K), [17] which was explained by the increase of the copper–copper distance and the change of the angles in the bridge fragment.

The copper complexes (VIIa) and (VIIb), obtained by the interaction of *S*-methyldithiocarbazide with salicylaldehyde (VII) and acetylacetone (VIIb), [28-32] as well as complexes with the thiosemicarbazones of *o*-hydroxyaldehydes (VIId) [30,31] and with tridentate ligands (VIIe), obtained by the condensation of diacetyl monoxime and its *O*-methyl

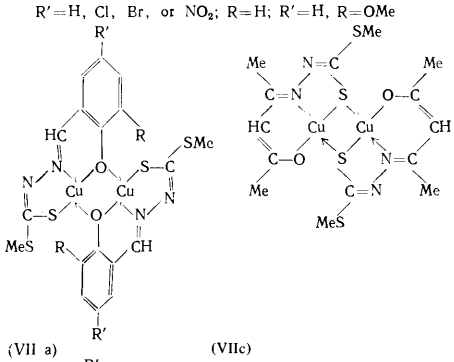
† Here *N* is the Avogadro number, $2J$ the exchange integral, μ_B the Bohr magneton, *k* the Boltzmann constant, *T* the absolute temperature, and $N\alpha$ the temperature-independent paramagnetism.

ether with methyl hydrazinethiocarboxylate (VIIf) have been investigated:

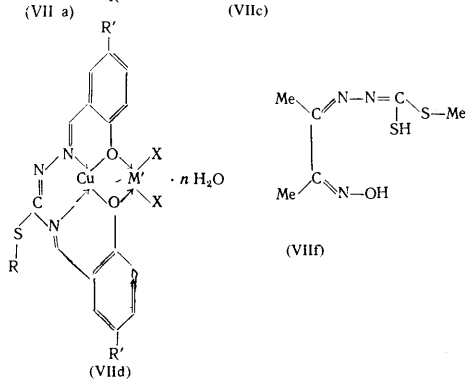


(VII) (VIIb)

R′=H, Cl, Br, or NO_2; R=H; R′=H, R=OMe



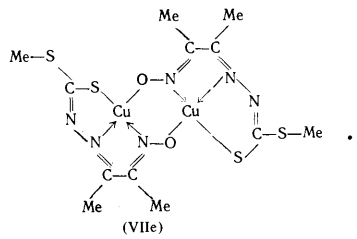
(VII a) (VIIc)



(VIIf)

(VIId)

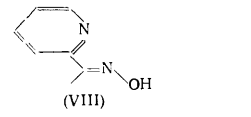
M′=Cu^{II}, Fe^{II}, or Zn^{II}; R=Me, or Et; R′=H, or Me; X=Cl, or Br



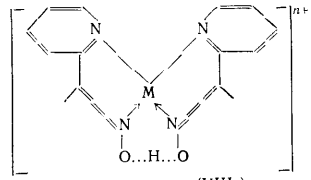
(VIIe)

Complexes (VIIe) are characterised by anomalous magnetic properties characteristic of exchange-bound clusters[32]; the compounds retain a similar structure when the sulphur atom is replaced by oxygen.

It has been found that complexes (VIIa) can manifest exchange interactions of both antiferromagnetic and ferromagnetic types depending on the nature of the substituents R and R′ (Table 2). An exchange interaction of the ferromagnetic type has also been observed for complex (VIIc) (μ_{eff} = 1.59–1.81 μ_B at 333–83 K). It has been suggested[29] that the indirect electronic influence of the substituents R and R′ and ultimately the change in the nature of the packing in the unit cell of the crystal have an effect here. Whereas complexes with an antiferromagnetic exchange interaction have a dimeric planar structure, complexes with a ferromagnetic exchange interaction consists of tetranuclear clusters in which copper atoms occupy the vertices of a distorted tetrahedron. The antiferromagnetic exchange interaction in complexes (VIId) depends on the nature of the substituents at the sulphur atom and in the benzene ring[30,31].



(VIII)



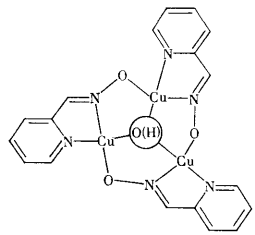
(VIIIa)

Table 2. Magnetic properties of copper complexes of types (VIIa) and (VIId).

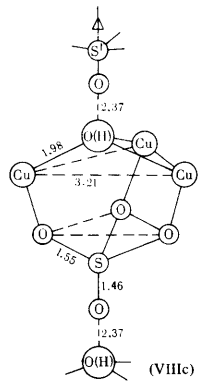
Type of complex	R′	R	X	T, K	μ_{eff}, μ_B
(VIIa)*	NO_2	H	—	333—83	2.02—2.43
(VIIa)	H	H	—	313—93	1.09—0.60
(VIIa)	H	OMe	—	373—193	1.01—0.40
(VIIa)	Cl	H	—	289	0.77
(VIIa)	Br	H	—	293	0.79
(VIId)	H	Me	—	288—78.8	1.60—0.67
(VIId)	H	Et	—	291.4—78.8	1.61—0.71
(VIId)	H	Me	Cl	288.3—78.8	1.60—0.67
(VIId)	H	Et	Cl	291.4—78.8	1.61—0.71
(VIId)	H	n-Bu	Cl	297.6—78.8	1.65—0.80
(VIId)	H	iso-Bu	Cl	297.6—78.2	1.62—0.99

* Ferromagnetic interaction; in the remaining cases the interaction is antiferromagnetic.

Depending on the method of synthesis of the complex, pyridinealdoxime (VIII) (HLig) can behave either as a bidentate ligand forming monomeric paramagnetic complexes[33] (VIIIa) or as a tridentate ligand forming coordination-unsaturated monomeric complexes, which are combined in the course of the reaction into trimeric molecules (VIIIb).



(VIIIb)



(VIIIc)

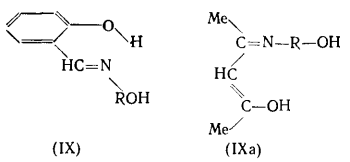
Several trinuclear copper complexes of this kind have been obtained: $[Cu_3Lig_3OH]X_2.H_2O$, where X = $\frac{1}{2}SO_4^{2-}$, I^-, NO_3^-, ClO_4^-, or OH^-; they all have anomalously low magnetic moments[34-37]. The study of the temperature dependence

of the magnetic susceptibility[37] as well as structural studies[36,37] confirmed the hypothesis that compounds of type (VIIIb) are trinuclear clusters in which copper ions are bound by an antiferromagnetic exchange interaction.

A cluster structure of the cation has been established for the complex $[Cu_3(C_6H_5N_3O_3)OH]SO_4.16H_2O$. The copper atoms are located at the corners of an equilateral triangle and the oxygen atom of the hydroxy-group is suspended over its centre at a distance of 0.71 Å. Each of the symmetrically linked aldoxime groups is a bridge group linking adjacent copper atoms. An interesting structural feature of this trimer is the fact that the three oxygen atoms of the sulphate ion augment the coordination polyhedron of each of the three copper atoms in the cluster to form a square pyramid. The trinuclear clusters are linked to one another via hydrogen bonds between the proton of the hydroxyl of one trimer and a non-coordinated oxygen atom in the sulpho-group of a neighbouring cluster.

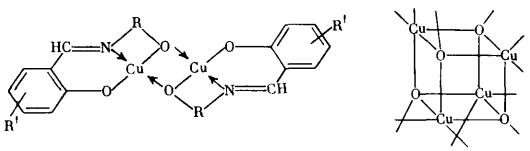
Similar trinuclear clusters with an antiferromagnetic exchange interaction have been obtained and investigated also with other analogous tridentate azomethine ligands[38-43].

The use of tridentate ligands of another type for the synthesis of complexes via the condensation of amino-alcohols with salicylaldehyde (IX) and acetylacetone (IXa),



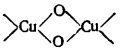
(IX) (IXa)

made it possible to follow clearly the influence on the nature of the exchange interaction in complexes (IXb) of the structural factor determined by the length and branching of the hydrocarbon group R.[43-47] It was found that only one compound among those investigated [R = $(CH_2)_3$] exhibits an exchange interaction of the antiferromagnetic type.



(IXb) (IXc)

The other compounds exhibit an exchange interaction of the ferromagnetic type (Table 3)[46].

A study of a complex of type (IXb) with R = $(CH_2)_3$ established tentatively its dimeric structure[45] and, in view of the influence of the transmission of the electronic effects of the substituents on the strength of the exchange interaction, it was postulated that the oxygen atoms of the alcohol and not the phenol are involved as bridge groups in the dimeric fragment  .[43] An X-ray diffraction study of the analogous copper complex (IXa), obtained from acetylacetone and having a very low magnetic moment (0.41 μ_B at room temperature) showed that this complex has a dimeric structure where the oxygen atoms of the alcohols function as the bridge groups[47]. In structures (IXa) and (IXb) the planes formed by the tetracoordinate environment of the copper ion and the tricoordinate environment of the oxygen bridge atoms are coplanar. It is suggested that this structural feature in fact accounts for the strong antiferromagnetic interaction [$-2J$ = 884 cm^{-1} and g = 2.20 were obtained for (IXb)][46] via an indirect exchange interaction π-mechanism [$Cu(3d_{xz})$ – $O(2p_\pi)$ – $Cu(3d_{yz})$], involving the d_{xz} and d_{yz} orbitals of the copper ion[47], rather than via the expected exchange via a σ-mechanism

$$\{Cu\,(3d_{x^2-y^2}) - O\,(2p_\sigma) - Cu\,(3d_{x^2-y^2})\}\ .$$

A decrease of the length of the hydrocarbon group to R = $(CH_2)_2$ leads to the formation of tetrameric exchange-bound clusters (IXc).[47] This structure explains the ferromagnetic nature of the exchange in complexes (IXb) (Table 3).

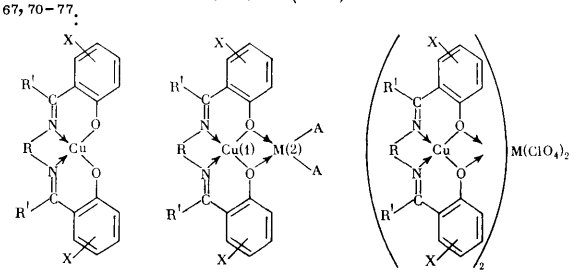
Table 3. Magnetic properties of complexes of type (IXb).

R	T, K	μ_{eff}, μ_B
$-CH_2-CH_2-CH_2$ *	295.7—150.1	0.43—0.07
$-CH_2-CH_2-$	291.4—76.4	1.88—2.09
$-CH_2-CH(Me)$	289.3—76.4	1.84—2.00
$-C(Me)_3$	286.1—76.4	2.09—2.41

* Antiferromagnetic interaction; in the remaining cases the interaction is ferromagnetic.

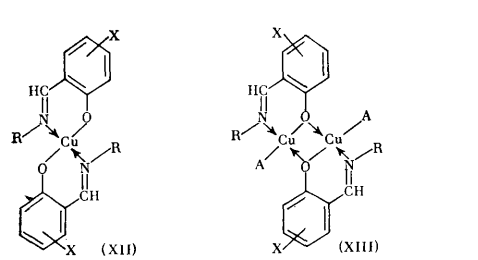
III. DI- AND POLY-NUCLEAR COMPLEXES BASED ON CHELATES WITH SCHIFF BASES AS LIGANDS

One of the commonest types of di- and poly-nuclear complexes with exchange interaction comprises compounds obtained by the insertion of a paramagnetic centre in the coordination unit of a chelate with a paramagnetic metal ion. These compounds are usually obtained either by the interaction of metal salts with chelates of tetradentate Schiff bases (X), whereupon di- and tri-nuclear complexes with a *cis*-structure (XI, a and b) are formed[48-66], or by the interaction of metal salts with the chelate (XII) formed by bidentate ligands, whereupon di- or poly-nuclear complexes with a *trans*-structure (XIII) are formed[44,49-51,53,54,57,59-67,70-77].



(X) (XIa) (XIb)

R = $(CH_2)_n$, n = 2, 3; R' = H, or Me; A = Cl, Br, or NO_3; X = H, 5-Cl, 5-Br, or 5,6-C_4H_4; M = Cu^{II}, Ni^{II}, Co^{II}, $Fe^{II,III}$, or Mn^{II}



(XII) (XIII)

R = Alk or Ar

X = H, 5-Cl, 5-Br, 5,6-C_4H_4, or 3-OMe; A = Cl or Br

Chelates with tridentate Schiff bases behave as neutral bidentate ligands coordinated to the metal atom of the MX_2 molecule via the two phenolic oxygen atoms, which is confirmed by the change in the vibration frequency of the Ph–O bond in the infrared spectra[53,54,67,77,83,85]. Dinuclear complexes of type (XIa, $n = 2$, M = Cu, A = Cl) are formed, the temperature dependence of the magnetic susceptibility of which obeys the Bleany–Bowers equation with $J < 0$. The exchange intergrals ($-2J$) and the g-factors are presented in Table 4.[52,61]

Table 4. The exchange integrals and g-factors for copper complexes of type (XIa).

X	R	R′	m*	A	$-2J$, cm^{-1}	g
H	$(CH_2)_2$	H	1	Cl	166	2.11
H	$(CH_2)_3$	H	0	Cl	49	2.14
H	CH_2-CH(Me)	H	0	Cl	106	2.15
H	o-C_6H_4	H	1	Cl	97	2.07
H	4-Me-C_6H_3	Me	1	Cl	91	2.08
H	$(CH_2)_2$	Me	0	Cl	236	2.35
H	$(CH_2)_3$	H	1	Cl	140	2.05
H	o-C_6H_4	H	1.2	Br	194	2.28
H	o-C_6H_4	H	1	Br	95	2.09
H	$(CH_2)_6$	H	0	Cl	139	2.29
5-Cl	$(CH_2)_2$	H	0	Cl	105	2.14
5,6-C_4H_4	$(CH_2)_2$	H	0	Cl	155	2.18
5-Cl	$(CH_2)_3$	H	0	Cl	204	2.35
5-Br	$(CH_2)_3$	H	0	Cl	195	2.35
H**	$(CH_2)_3$	H	1	Cl	55	1.87
H***	$(CH_2)_3$	H	2	Cl	24	1.92

* m is the number of water molecules.
** M = Fe^{III}.
*** M = Mn^{II}.

It has been noted in a number of studies[49,53,54,78,80] that the two metal atoms Cu(1) and M(2) in dinuclear complexes of type (XIa) are in different environments: Cu(1) in a square-planar environment and M(2) in a pseudotetrahedral environment (Fig. 1). The symmetry of the M(2) coordination unit depends significantly on the number of R = $(CH_2)_n$ bridge groups[75]. In complexes (XIa) with $n = 2$ the M(2) unit has the structure of a distorted tetragonal pyramid (as a result of the additional coordination of chlorine from a neighbouring molecule); for complexes with $n = 3$, M(2) has a pseudotetrahedral stereochemistry. The magnetic properties of complexes (XIb), forming trinuclear compounds, have been interpreted on the assumption that the metal atoms are located at the vertices of an equilateral triangle[50], the antiferromagnetic properties increasing in the sequence Co < Ni < Cu.[51] The relative stability of complexes (XIb) and the energy of d–d transitions were found to vary in parallel with the extent of the antiferromagnetic interaction, which can be accounted for by the successive increase of the tetragonal distortion of the M(2) coordination unit in many copper, nickel, and cobalt complexes (Fig. 1),[49,53,54]. However, one must bear in mind that this explanation is not always correct owing to the possibility of an increase of the coordination number of Cu(2) to five, and M(2) can partly displace copper from the "planar" complex.

It has been shown[60,62,66] that the interaction of complexes [X, R = $(CH_2)_2$, M = Cu^{II}, Ni^{II}, Co^{II}, or Fe^{III}] with the Lewis acids SnX_2, SnX_4, $TiCl_4$, SbX_5, $InCl_3$, $CaCl_2$, PCl_3, and $AsCl_3$ (where X = Cl or Bi) leads to the formation of dinuclear complexes in which the initial chelate with a tetradentate Schiff base can exchange the metal with the Lewis acid, forming various structures. Only when cyclic polymeric-tetrahedral adducts (XIa, M = Co or Cu) and polymeric-octahedral adducts (XIa, M = Ni^{II}) are formed with PCl_3 and $AsCl_3$, is the non-linearity of the temperature dependence of the reciprocal of the magnetic susceptibility attributed to the antiferromagnetic interaction. For the compound with PCl_3, a satisfactory agreement is observed between the experimental susceptibility and the value calculated using the linear chain model ($g = 2.11$, $2J = -55$ cm^{-1}).[65]

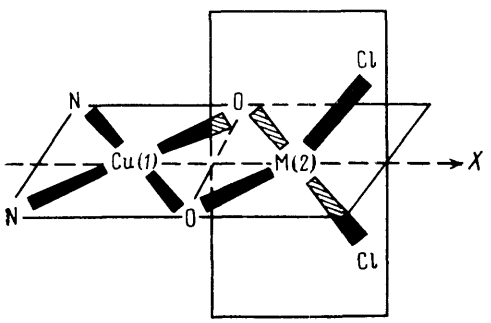


Figure 1. A fragment of the structure of a dinuclear complex of type (XIa).

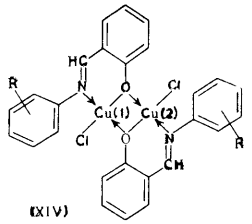
In dinuclear complexes (XIa, M = Ni), containing a water molecule, the exchange interaction can exhibit ferromagnetic features[72].

When Lewis acids interact with copper(II), cobalt(II), and nickel(II) complexes of type (XII), there is a possibility, judging from the changes in the infrared and electronic spectra, of the cleavage of the metal chelate ring in the initial chelate, which leads to the formation of complex dinuclear structures[83–86]. The effective magnetic moments of the above compounds, calculated per atom of the paramagnetic metal, have normal values. However, the coordination-unsaturated compounds formed as a result of the cleavage of the metal-chelate ring interact with one another and not with the Lewis acid and give rise to insignificant amounts of compounds with exchange-bound [electron] pairs as impurities in the main product, as shown by the appearance of a broad absorption band in the EPR spectra of the copper complexes in the region corresponding to weak fields.

Dinuclear copper complexes based on chelates with bidentate ligands (XIII) also manifest an appreciable exchange interaction of the antiferromagnetic type. The exchange integrals ($-2J$) and average g-factors of some of these are presented in Table 5.

In the dinuclear ecomplexes (XIa) and (XIII) the Cu–Cu distance is ~3 Å,[78–81] as in the copper complex of N-(2-hydroxyphenyl)acetylacetoneimine[13,14]. In the dimeric copper complex of the tetradentate N,N'-bis-(2-hydroxyethyl)acetylacetonediimine the Cu–Cu distance increases to 4.99 Å and the exchange integral is $2J = -94$ cm^{-1}.[82] In the trinuclear complexes $(NiL_2)_2.Ni(NO_3)_2$ there is a weak ferromagnetic interaction[71].

Systematic studies of dinuclear complexes of type (XIV)



(XIV)

showed[69,70,75-77] that, as in the analogous dinuclear complexes of copper halides with pyridine *N*-oxides[73,74], the substituents R have a weak influence on the energy of the *d–d* transitions and the effective magnetic moments. Nevertheless the bands corresponding to the *d–d* transitions in dimeric complexes with *ortho*-substituents are shown at shorter wavelengths than for the corresponding complexes with *meta*- and *para*-substituents (Fig. 2), which is believed to correspond to a decrease of μeff in dinuclear complexes with *ortho*-substituents compared with complexes having *meta*- and *para*-substituents[69,75,76].

Table 5. The exchange integrals ($-2J$) and g-factors for complexes of type (XIII).

R	X	A	$-2J$, cm^{-1}	g	Refs.
Me	H	Cl	149	2.17	55
CH_2Me	H	Cl	240	2.18	55
$(CH_2)_2Me$	H	Cl	255	2.08	55
$(CH_2)_3Me$	H	Cl	205	2.14	55
$(CH_2)_5Me$	H	Cl	188	2.12	55
$(CH_2)_7Me$	H	Cl	180	2.14	55
$CH_2CH(Me)_2$	H	Cl	245	2.12	55
$CH(Me)_2$	H	Cl	145	2.17	55
$CH(Me)CH_2Me$	H	Cl	155	2.11	55
C_6H_{11}	H	Cl	220	2.18	55
Ph	H	Cl	180	2.16	55
CH_2Me	5-Cl	Cl	140	2.14	57
$(CH_2)_2Me$	5-Cl	Cl	188	2.35	57
$CH(Me)_2$	5-Cl	Cl	136	2.38	57
Me	5-Br	Cl	220	2.23	57
CH_2Me	5-Br	Cl	200	2.30	57
$CH(Me)_2$	5-Br	Cl	195	2.22	57
Me	5,6-C_4H_4	Br	175	2.20	57
Me	5-Cl	Br	146	2.20	57
Me	5-Br	Br	140	2.35	57
Me	5-Cl	Cl	280	2.15	57
Me	5,6-C_4H_4	Cl	173	2.14	57
Me	H	NO_3	280	2.12	71
CH_2Me	H	NO_3	83	2.14	71
$(CH_2)_2Me$	H	NO_3	350	2.20	71
$(CH_2)_3Me$	H	NO_3	191	2.18	71
C_6H_{11}	H	NO_3	208	2.12	71
CH_2Ph	H	NO_3	120	2.08	71
Me	3-OMe	NO_3	43	2.17	71
C_6H_{11}	5,6-C_4H_4	Cl	130	2.10	57
C_6H_{11}	5-Cl	Cl	250	2.20	57
C_6H_{11}	5-Br	Cl	215	2.32	57
C_5H_9	5,6-C_4H_4	Cl	160	2.20	57
C_5H_9	5-Cl	Cl	132	2.28	57
C_5H_9	5-Br	Cl	210	2.38	57
$CH(Me)_2$	5,6-C_4H_4	Cl	97	2.30	57
$(CH_2)_2(Me)$	5-Br	Cl	180	2.26	57

There is a linear relation between the magnetic moment and the position of the band due to the *d–d* transition (Fig. 3)[75]. The same type of relation has been found also for dinuclear complexes of copper with tetradentate Schiff bases of type (XIa).[53,54] It has been suggested[77] that this type of linear relation indicates a transition from a distorted pseudotetrahedral configuration to a planar configuration when *ortho*-substituents are introduced. An increasing degree of planarity leads to a hypsochromic shift of the *d–d* band and to a decrease of the magnetic moment owing to the appreciable overlap of the metal atom orbitals with the orbitals of the bridging oxygen atoms. A similar effect involving the "flattening" of the coordination unit following the introduction of *ortho*-substituents has been observed for monomeric copper complexes of salicylidenearylamines[6] and can be accounted for by the steric conditions arising after the introduction of *ortho*-substituents, since the benzene rings both in copper complexes of salicylideneaniline derivatives and in the dinuclear complexes investigated are located at an angle of 60° relative to the plane of the coordination unit.

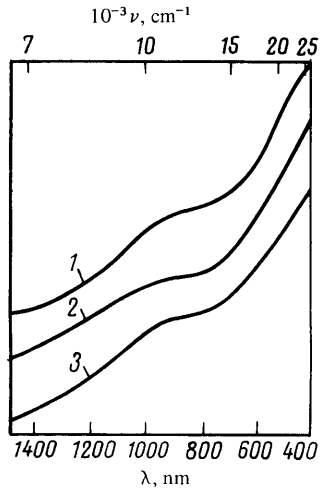


Figure 2. Diffuse reflection spectra of complexes (XIV); R: 1) 2-Me; 2) 3-Me; 3) 4-Me.

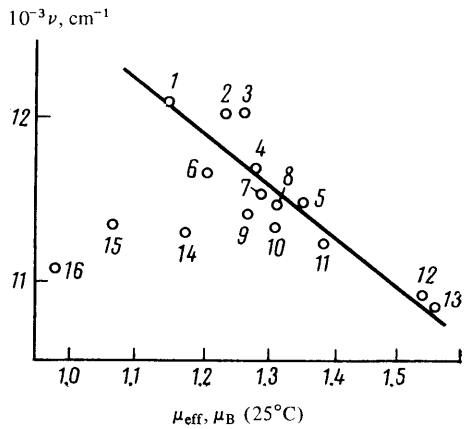


Figure 3. Dependence of the position of the *d–d* transition bands and μeff (at 25°C) on the substituent R for complexes of type (XIV); R: 1) 2-Cl; 2) 2-Me; 3) 3-Cl; 4) 2,4-Me_2; 5) 2,6-Me_2; 6) 2,6-Cl_2; 7) 3,4-Cl_2; 8) 4-Me; 9) 3,5-Cl_2; 10) 4-Cl; 11) H; 12) 3-NO_2; 13) 3-Me; 14) 2,5-Cl_2; 15) 2-NO_2; 16) 4-NO_2.

An analogous relation has been established for dinuclear complexes (XIII, R = alkyl) with alkyl substituents. As for mononuclear chelates, the replacement of a straight-chain alkyl group by a bulky branched group (for example, the replacement of n-C_3H_7 by iso-C_3H_7 or of n-C_4H_9 by t-C_4H_9) leads, with rare exceptions (R = Me),[81] to a tetrahedral distortion of the geometry and to a corresponding increase of μ_{eff} and a decrease of the frequency of the d–d transition[77].

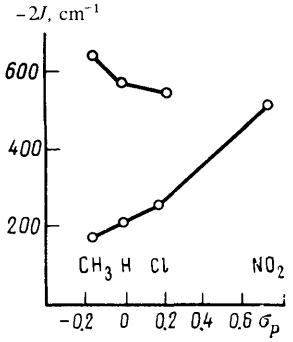


Figure 4. Dependence of the exchange integral on the Hammett constants σ_p for complexes of type (XIXa).

Thus there is a direct relation between the degree of tetrahedral distortion of the coordination unit in dinuclear complexes of type (XIII) and the decrease of the antiferromagnetic interaction between pairs of copper atoms[81]. The dihedral angles τ between the planes in which the copper atoms of the two halves of the dimeric molecules of (XIII) are located have been compared[81] with the integrals $-2J$. The values of τ are respectively 33.1°, 35.7°, 35.5°, and 39.3° for complexes with the following substituents: A = Cl, X = H, and R = Et; A = Br, X = H, and R = Et; A = Br, R = n-C_4H_9, and X = 5-Cl; A = Cl, X = H, and R = Me; the corresponding values of $-2J$ are 240, 205, 220, and 146 cm^{-1}.

If the structure of the complexes differs from the pseudotetrahedral structure, a linear relation is not observed between μ_{eff} and the d–d transition frequency. Depending on the conditions of synthesis and the nature of the alkyl substituent introduced into the aldehyde ring of the liquid, complexes (XIII) with different stereochemistries of the coordination units can be obtained[77]. The above compounds have been classified on the basis of the results: (1) type B—pseudotetrahedron; (2) type YG—square pyramid with a weak distortion in the direction of a trigonal-pyramidal configuration; (3) type Y—trigonal bipyramid with a weak distortion in the direction of a square-pyramidal configuration; (4) type Y'—trigonal bipyramid with a large distortion in the direction of a square-pyramidal configuration.

Naturally, for different stereochemical configurations, the dependence of μ_{eff} on the d–d transition frequency is different[77]. For regular square-pyramidal dinuclear structures, antiferromagnetic exchange via oxygen bridges should take place, as for planar complexes:

$$3d_{x^2-y^2}\,[\mathrm{Cu}\,(1)] - p_\sigma\,(\mathrm{O}) - 3d_{x^2-y^2}\,[\mathrm{Cu}\,(2)] \quad \sigma\text{-mechanism};$$
$$3d_{xz}\,[\mathrm{Cu}\,(1)] - p_\pi\,(\mathrm{O}) - 3d_{yz}\,[\mathrm{Cu}\,(2)] \quad \pi\text{-mechanism}.$$

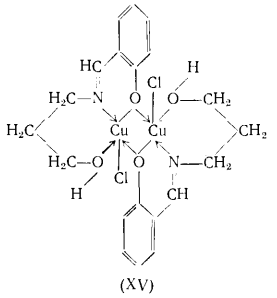
For regular trigonal-bipyramidal structures, antiferromagnetic exchange takes place as follows:

$$3d_{x^2-y^2}\,[\mathrm{Cu}\,(1)] - p_\sigma\,(\mathrm{O}) - 3d_{z^2}\,[\mathrm{Cu}\,(2)] \quad \sigma\text{-mechanism},$$
$$3d_{xy}\,[\mathrm{Cu}\,(1)] - p_\pi\,(\mathrm{O}) - 3d_{yz}\,[\mathrm{Cu}\,(2)] \quad \pi\text{-mechanism}.$$

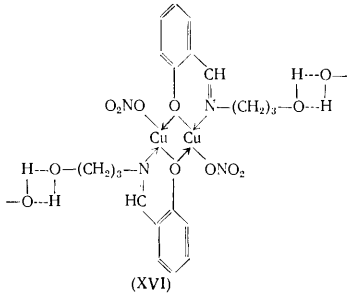
This approach makes it possible to infer the nature of the antiferromagnetic interaction and the symmetry of the coordination unit on the basis of the study of the dependence of the d–d transition energy on the effective magnetic moment in systematically selected series of complexes.

The complexes Cu(SalNROH)X (X = Cl, NO_3, or ClO_4), which are obtained by the interaction of copper salts and copper chelates with N-hydroxyalkylsalicylideneamines (IX), can have different compositions, structures, and magnetic properties depending on the method of synthesis, the nature of the anion, and the steric conditions (determined by the length and degree of branching of the hydroxyalkyl group)[46,87,88].

Whereas antiferromagnetic interactions of different strengths are observed for complexes with R = $(CH_2)_2$, $(CH_2)_3$, or CH_2–CH(Me) and X = Cl or ClO_4, when a nitro-group is introduced into the aldehyde ring of the ligand [for the complex with R = $(CH_2)_2$ and X = Cl] and with increase of the degree of branching of the group [R = Me–CH(Me), X = Cl or NO_2], these complexes behave as the usual paramagnetic materials[88]. It is suggested that the nature of the exchange interaction in the dimeric compounds (XV) is associated with the different degrees of distortion of the coordination unit as a function of R. For compounds with R = $-(CH_2)_3-$ and X = Cl, X-ray diffraction analysis revealed a distorted trigonal-pyramidal structure (XV):[89,90]



(XV)



(XVI)

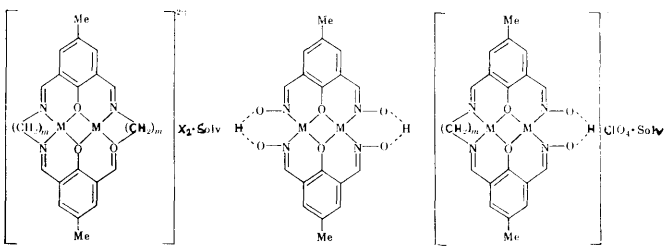
These are thus complexes of the second type, obtained on the basis of 3-hydroxy-N-propylsalicyclideneamines [the first type is a dimer (IXb) with a strong exchange interaction]. It has been shown[87] that these two types of complexes can undergo an interconversion under certain conditions. It has been suggested[87] that interaction with copper nitrate gives rise to compound (XVI), in which the alcoholic group is not deprotonated and is not coordinated to the metal, but forms a polymer chain via hydrogen bonding. An antiferromagnetic type of exchange is also

characteristic of complex (XVI), but its magnetic properties cannot be interpreted unambiguously[87,91].

The influence of the structural factor on the magnetic properties of copper compounds with *N*-hydroxyethyl-5-R-salicylaldimines of type (XV, R = H, Me, Cl, or NO_2) has been investigated[88]. A dinuclear structure with chloride bridges has been established for $[Cu(5\text{-}RSaL.NEtOH)Cl]_2$ with R = H or Me; a dinuclear structure with a phenolic oxygen as the bridge has been found for Cu-(5-MeSal. .NEtOH)Br.0.1 DMF (DMF = dimethylformamide); a linear trinuclear structure (also with the phenolic oxygen as the bridge) has been determined for $Cu_3(Sal.N.EtOH)_2Cl_4$. .2EtOH. The magnetic properties of these complexes are presented in Table 6. The form of the temperature dependence of the magnetic susceptibility permits a polymeric chain structure of $Cu_2(5\text{-}MeSalNEtOH)Cl_3.0.5H_2O$. For other complexes of this type, the structural data have also been correlated with their magnetic properties (Table 6).

IV. DINUCLEAR COMPLEXES WITH POLYDENTATE DIMERISING LIGANDS

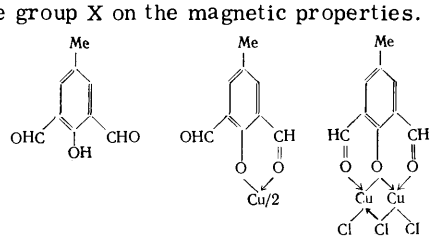
The azomethine derivatives (XVIII) and (XIX), obtained on the basis of 3-formyl-5-methylsalicylaldehyde (XVII), are typical dimerising ligands[92,93].



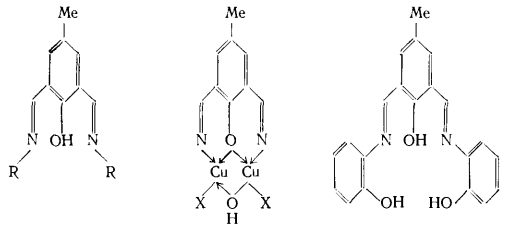
(XXa) (XXb) (XXc)

M = Cu, Ni, or Co; X = Cl or ClO_4; Solv = H_2O; m = 2, 3 . M = Cu or Ni M = Cu or Ni; Solv = DMF or H_2O

The effective magnetic moments of the mononuclear complex (XVIIa) and the dinuclear complex (XVIIb) are respectively 1.81 and 1.58 μ_B, while the μ_{eff} for dinuclear azomethine complexes of type (XVIIIa) are 0.8–1.29 μ_B at room temperature, depending on the substituent R.[93] Hence one may conclude that azomethine ligands give rise to dinuclear complexes (XVIIIa) with a stronger exchange interaction than complexes (XVIIb). These compounds were described for the first time by Robson[92], who investigated complexes (XIXa) with the ligand (XIX). The structure of (XIXa) has been confirmed by X-ray diffraction[92]. Several types of complexes (XXIa) have been synthesised by condensing (XVII) with various amines and investigated[92,94–97]. Comparison of complexes of type (XIXa) with different bridge groups but with identical Z (nos. 1–7, Table 7) reveals the influence of the nature of the bridge group X on the magnetic properties.

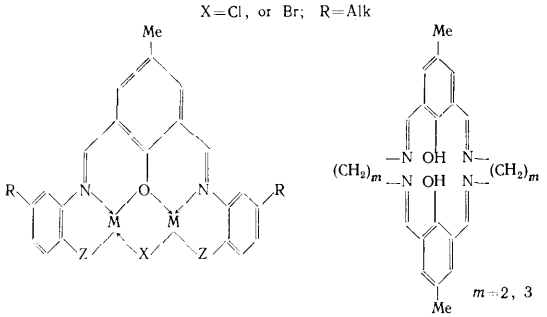


(XVII) (XVIIa) (XVIIb)



(XVIII) (XVIIIa) (XIX)

X=Cl, or Br; R=Alk



(XIXa) (XX)

X: 1/2O_2, OMe, OEt, OH, N_3, $OCH_2C_6H_5$, $C_3H_3N_2$, Cl or (OCH_2CH_2OMe); Z = O or S; M = Cu or VO; R = H, Cl, Me, or NO_2.

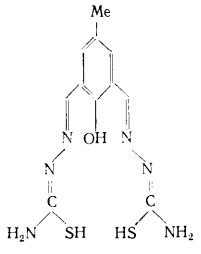
Table 6. The exchange integrals ($-2J$), magnetic moments (μ_{eff}), and g-factors for the complexes $Cu_n(5R'.SalNROH)_m.X.Solv$.

n	m	R^1	X	R	Solv	T, K	μ_{eff}, μ_B	$-2J$, cm^{-1}	g	Refs.
1	1	H	Cl	$(CH_2)_2$	—	76.4—289.7	1.0—1.63	124	2.10	46
						118.3—309.4	1.79—1.82	10	2.06	87
1	1	NO_2	Cl		—	76.2—291.8	1.79—1.80	—	—	46
1	1	H	Cl	$(CH_2)_2$						
1	1	H	Cl	$CH_2CH(Me)$	H_2O	76.2—299.7	1.82—1.83	—	—	46
1	1	H	Cl	$(CH_2)_3$	—	96.3—309.6	0.04—1.05	504	2.20	46
1	1	H	Cl	$(CH_2)_3OMe$ *	—	76.3—287.7	0.07—1.00	491	2.18	46
1	1	H	NO_3	$(CH_2)_2$	—	81.0—300.5	1.81—1.80	—	—	46
						86.0—320.5	1.66—1.85	30	—	87
1	1	H	NO_3	$CH_2CH(Me)$	—	76.4—298.1	1.80—1.83	—	—	46
1	1	H	NO_3	$(CH_2)_3$	—	76.4—301.3	1.80—1.81	—	—	46
1	1	H	ClO_4	$(CH_2)_2$	H_2O	76.4—292.0	0.16—1.27	332	2.10	46
1	1	H	ClO_4	$(CH_2)_2$	2DMF	76.2—290.5	1.86—1.86	—	—	46
1	1	H	ClO_4	$CH_2CH(Me)$	EtOH	76.2—294.8	0.07—1.18	403	2.15	46
1	1	H	ClO_4	$CH_2CH(Me)$	2DMF	76.2—291.2	1.82—1.81	—	—	46
2	2	H	$2NO_3$	$(CH_2)_3$	—	114.0—345.3	0.47—1.36	320	2.08	87
2	2	H	2Cl	$(CH_2)_3$	—	138.0—387.5	0.30—1.20	470	2.09	87
1	1	Cl	NO_3	(CH_2)	—	79.0—345.3	1.25—1.59	—	—	87
1	1	Cl	Cl	(CH_2)		77.0—381.5	1.74—1.80	10	2.06	87
3	2	H	4Cl	$(CH_2)_2$	2EtOH	76.3—299.9	1.20—1.68	60	2.18	88
1	1	H	Br	$(CH_2)_2$	—	76.3—289.6	1.76—1.78	—	—	88
1	1	Me	Cl	$(CH_2)_2$	—	76.3—286.1	1.09—1.64	55	2.06	88
1	1	Me	Cl	$(CH_2)_2$	1/2·EtOH	76.4—286.0	1.79—1.82	—	—	88
2	1	Me	3Cl	$(CH_2)_2$	1/2 H_2O	76.4—287.4	0.84—1.49	83	2.13	88
1	1	Me	Br	$(CH_2)_2$	1/2 H_2O	76.3—286.5	1.71—1.76	—	—	88
1	1	Me	Br	$(CH_2)_2$	0.1DMF	76.3—288.7	0.16—0.83	290	2.20	88
1	1	Cl	Cl	$(CH_2)_2$	—	76.3—287.5	1.75—1.79	—	—	88
1	1	Cl	Br	$(CH_2)_2$	—	76.4—286.5	1.73—1.76	—	—	88
1	1	NO_2	Br	$(CH_2)_2$	—	76.3—286.5	1.72—1.76	—	—	88

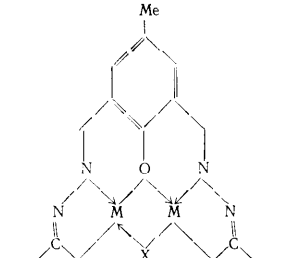
* Compound having the general formula $Cu_n(5\text{-}R'.Sal.N.ROMe)_m.X.Solv$.

On the other hand, when complexes with the same group but different Z are compared (Nos. 2 and 8, Table 7), the enhancement of the exchange interaction following the replacement of oxygen by sulphur in the coordination unit is clearly manifested, and the ligand residue does not apparently have a significant influence in these complexes

on the nature of the exchange interaction, as shown by a comparison of the properties of complexes of different types [(XIXa) and (XXIa)] but with the same bridge groups X and identical Z (Nos. 8 and 9 and 10 and 11, Table 7).



(XXI)



(XXIa)

M=Cu^{II} or Ni^{II}; X=$C_3H_3N_2$, N_3 or Cl .

Table 7. The values of μ^*_{eff}, exchange integrals, and g-factors for complexes.

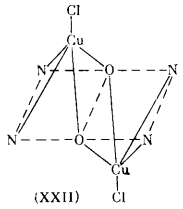
No.	Type of complex	M	Z	R	X	μ_{eff}, μ_B	$-2J$, cm^{-1}	g	Refs.
1	(XIX)	Cu	0	H	OMe	0.97	385	2.1	92
2	(XIXa)	Cu	0	H	$C_3H_3N_2$	1.40	230	2.1	92
3	(XIXa)	Cu	0	H	OEt	0.85	—	—	94
4	(XIXa)	Cu	0	H	OCH_2CH_2OMe	0.77	—	—	94
5	(XIXa)	Cu	0	H	OCH_2Ph	0.60	—	—	94
6	(XIXa)	Cu	0	H	OH	1.17	—	—	94
7	(XIXa)	Cu	0	H	OH	0.98	—	—	94
8	(XIXa)	Cu	S	H	$C_3H_3N_2$	1.20	372	2.0	95
9	(XIXa)	Cu	S	H	N_3	0.70	—	—	95
10	(XXIa)	Cu	—	—	$C_3H_3N_2$	1.20	414	2.2	95
11	(XXIa)	Cu	—		N_3	1.00	472	2.0	95
12	(XXIa)	Cu	—		Cl	1.20	430	2.3	95
13	(XIXa)	VO	0	Me	OMe	1.46	180	1.87	98
14	(XIXa)	VO	0	H	OMe	1.37	230	1.86	98
15	(XIXa)	VO	0	Cl	OMe	1.25	280	1.81	98
16	(XIXa)	VO	0	NO_2	OMe	0.85	545	1.95	98
17	(XIXa)	Cu	0	Me	OMe	0.70	655	2.15	98
18	(XIXa)	Cu	0	H	OMe	0.88	570	2.15	98
19	(XIXa)	Cu	0	Cl	OMe	1.04	555	2.15	98
20	(XIXa)	Cu	0	NO_2	OMe	1.18	—	—	98
21**	(XXa)	Cu	—	—	Cl	0.70—0.04	—	—	96
22***	(XXa)	Cu	—	—	ClO_4	0.58—0.10	—	—	96

* At room temperature.
** In the range 351–89 K.
*** In the range 286–90 K.

According to a hypothesis[95], confirmed by X-ray diffraction analysis of analogous complexes[97], compounds (XIXa) have a tetrameric structure and the change in magnetic properties is to a large extent determined by the distortion of the coordination unit on formation of the tetramers.

It is of interest to compare the behaviour of dinuclear complexes of type (XIXa) having identical Z and X (Z = O, X = OMe) but variable R. [98] A certain correspondence between the electronic influence of the substituents R (Hammett σ_p constants) and the quantity $-2J$ (Fig. 4 and Nos. 13–20 in Table 7) has been explained[98] by the fact that the overlap of the d_{xy} orbitals in the vanadyl complexes increases in the sequence R = Me < H < Cl in parallel with the deviation of the vanadium atom from the plane of the coordination unit. On the other hand, $-2J$ for tetragonal copper complexes is influenced to the greatest extent by the change in the equatorial bonds involved in the exchange. This is why $-2J$ decreases with enhancement of the electron-accepting properties of the substituent R, leading to the combination of electron density at the phenolic oxygen bridge. Complexes (XIXa) with R = NO_2 for which a polymeric structure has been established, constitute a special case.

A strong antiferromagnetic interaction has been observed for complexes (XXa) (Nos. 13 and 14, Table 8). The square-pyramidal structure (XXII)



(XXII)

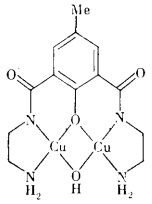
was assigned to them on the basis of X-ray diffraction studies of similar compounds[96].

Table 8. The values of μ_{eff}, exchange integrals, and g-factors for complexes.

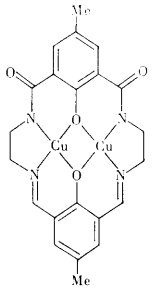
No.	Type of complex	m	R	X	M^{2+}	T, K	μ_{eff}, μ_B	$-2J$, cm^{-1}	g	Refs.
1	(XXIV)	—	H	OH	Cu	76.2—283.0	0.07—1.05	447	2.16	103
2	(XXIV)	—	H	Cl	Cu	76.2—289.8	1.52—1.71	—	—	103
3	(XXIV)	—	H	Br	Cu	76.2—288.3	1.70—1.76	—	—	103
4	(XXIV)	—	Me	Cl	Cu	76.3—285.3	1.45—1.72	—	—	103
5	(XXV)	—	Me	Cl	Cu	299.3	1.61	143	2.10	104
6	(XXV)	—	Me	Br	Cu	301.1	1.61	155	2.10	104
7	(XXV)	—	Me	OH	Cu	291.8	1.29	330	2.11	104
8	(XXV)	—	Et	Cl	Cu	302.6	1.66	123	2.10	104
9	(XXV)	—	Et	Br	Cu	291.6	1.68	125	2.16	104
10	(XXV)	—	Et	OH	Cu	303.4	0.49	865	2.15	104
11	(XXb)	—	—	—	Cu	room	0.59	—	—	106
12	(XXb)	—	—	—	Ni	room	2.87	—	—	106
13	(XXc)		—	—	Cu	room	0.59	—	—	106
14	(XXc)		—	—	Cu	room	0.61	725	2.10	106
15	(XXc)*	—	—	—	Cu	room	2.25	—	—	106
16	(XXIIIb)	—	Me	—	Cu	297.7	0.68	720	2.20	99
17	(XXIIIb)	—	Et	—	Cu	291.6	0.66	715	2.20	99
18	(XXIIIb)	—	C_2H_4OH	—	Cu	297.7	0.54	820	2.20	99
19	(XXIIIb)	—	n-Pr	—	Cu	294.2	0.66	725	2.20	99
20	(XXIIIb)	—	n-Bu	—	Cu	296.6	0.71	705	2.20	99
21	(XXIIIb)	—	iso-Bu	—	Cu	294.1	0.63	735	2.17	99
22	(XXIIIb)	—	s-Bu	—	Cu	295.4	0.63	750	2.20	99
23	(XXIIIb)	—	Me	—	Ni	198.7—87.0	3.14—2.76	—	—	99
24	(XXIIIb)	—	Et	—	Ni	293.0—77.5	3.10—2.64	—	—	99
25	(XXIIIb)	—	C_2H_4OH	—	Ni	291.7—83.5	3.06—2.74	—	—	99
26	(XXIIIb)	—	n-Bu	—	Ni	296.6—87.1	3.17—2.72	—	—	99
27	(XXV)	—	Me	NCS	Cu	298.0	1.57	—	2.18	105
28	(XXV)	—	Et	NCS	Cu	297.0	1.62	—	2.17	105

* The value of μeff was found on the assumption that one nickel atom is diamagnetic.

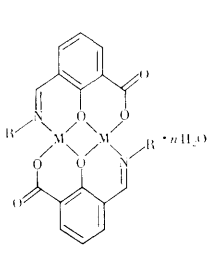
Dinuclear complexes (XXIIIa) with analogous ligands (XXIII) have been synthesised[100]:



(XXIII)



(XXIIIa)

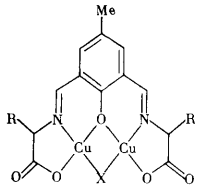


(XXIIIb)

M = Cu^{II}, or Ni^{II}; R = Alk .

It has been shown that the exchange interaction is greatly intensified on passing from (XXIII) (μ_{eff} = 1.14 μ_B at T_{room}) to (XXIIIa) (μ_{eff} = 0.79 μ_B at T_{room}), because the system is more rigid and because of the introduction of the conjugated azomethine fragment. At the same time, dimeric complexes (XXIIIb) have been obtained on the basis of 3-formylsalicylic acid[99]; the parameters characterising the exchange interaction in (XXIIIb) were compared with the values for the analogous complexes (XIII). The authors[99] emphasise that the substituents R in compounds (XXIIIb) have a weaker steric influence than in (XIII).

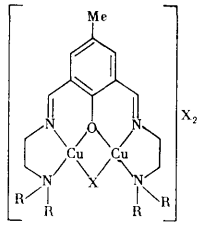
Complexes (XXb) and (XXIV) have been synthesised and investigated[101-103]:



(XXIV)

R = Me, X = Cl;

R = H, X = Cl, Br, or OH



(XXV)

R = Me, Et, or H;

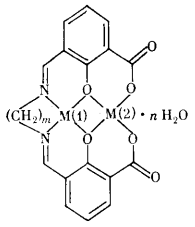
X = Cl, Br, OH, or NSC

A significant change in their magnetic properties was demonstrated on varying the bridge group X [101-103] (Table 8): for X = OH, a strong antiferromagnetic interaction is observed, while for X = Cl or Br, it is significantly less intense[101-103]. Since the Cu–Cu distance in a dimeric molecule is 3.4 Å, an indirect exchange interaction via the bridge groups is observed. It is suggested that this change in magnetic properties indicates a change in the extent of the indirect interaction of the bridge groups in the sequence OH $\gtrsim$ Cl $\simeq$ Br. At the same time the authors[103] assume that the high effective magnetic moments of compound Nos. 5, 6, and 7 in Table 8 can be due to the distortion of the plane of the coordination unit.

An analogous effect of bridge groups was investigated in greater detail in relation to complexes of type (XXV).[104] It was shown on the basis of the temperature variation of the magnetic susceptibility that the antiferromagnetic exchange interaction between two copper atoms diminishes in the sequence OH $\geqslant$ Br > Cl for the same contribution of the phenolic oxygen to the indirect exchange. However, one must bear in mind (Nos. 8–10, Table 8)[104] the role of the geometrical factor. It has been postulated[104] that the above complexes with a chloride anion have a tetragonal-pyramidal structure and, judging from the electronic spectra, complexes (XXV) with X = OH have a structure different to that of complexes with X = Cl or Br. Indeed the introduction of the group X = SCN leads[105] to the formation of tetrameric structures in which two dimers are linked to form a tetramer via intermolecular S...Cu bonds. The Cu–Cu interaction in the dimers remains antiferromagnetic.

A strong exchange interaction has been observed also for complexes of type (XX, b and c) (Nos. 11–15, Table 8)[106]. A tetragonal-pyramidal structure was also attributed to them. The enhancement of the exchange interaction between them is explained by a more rigid matrix due to the ligand.

Polydentate ligands based on 3-formylsalicylaldehyde[107,108] have been used to obtain di- and poly-nuclear complexes whose molecules contain two different metals (Cu and Ni).[107,111] Bimetallic complexes of type (XXa), each molecule of which contains Co^{II} and Co^{III},[110] as well as complexes of type (XXVI) based on 3-formylsalicylic acid[110-112] have been synthesised.



M(1) = Cu, m = 3, M(1) = Cu, n = 1;

m = 2, M(2) = Co, Fe, Mn, Ni, UO_2, or Th/2; n = 0–3.

(XXVI)

It is noteworthy that the possibilities of complexes of this series have been by no means exhausted and, on the basis of studies carried out hitherto[92-111], it is difficult to make general conclusions concerning the correlation between the structure, the nature of the bridge groups, and the exchange interaction. This is because the structures of these compounds have been inadequately elucidated and the conclusion that the complexes have the same structures, reached when a systematic comparison is made of series of such complexes, are mainly based on the analogy with the known structural data for other similar systems.

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The Hydride Addition of Organohydrosiloxanes to Compounds with a Multiple Carbon-Carbon Bond

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Reactions leading to the formation of an Si-C bond—the hydrosilylation of unsaturated organic compounds by organohydrosiloxanes and the hydride addition of organohydrosiloxanes to organosilicon compounds containing multiple carbon-carbon bonds—are examined. Factors influencing the course of the reaction and the properties of the addition products are discussed. The bibliography includes 153 references.

CONTENTS

I. Introduction 657
II. The hydride addition of organohydrosiloxanes to compounds with a multiple carbon-carbon bond 657
III. The hydride polyaddition of organodihydrosiloxanes to di- and polyfunctional unsaturated compounds 660
IV. The principal factors influencing the course of the hydride addition reaction 662

I. INTRODUCTION

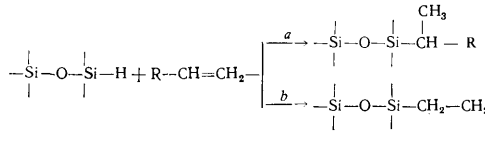
Hydride addition reactions are common in organic and organoelemental chemistry. Using these reactions, a wide variety of numerous organosilicon compounds have been synthesised. The addition of hydrogen-containing organosilicon compounds to compounds with a multiple carbon–carbon bond, the so-called hydride addition or hydrosilylation reaction, constitutes one of the methods for the formation of an Si–C bond[1-3].

The hydride addition reaction has been widely used recently not only for the synthesis of organosilicon monomers and oligomers but also for the conversion of linear and branched organoelemental polymers into polymers with a network structure. The hydride addition reaction has also acquired great importance for the synthesis of polycarbo-organosiloxanes.

Since studies on the hydride addition of organohydrosiloxanes to various organic and organosilicon unsaturated compounds published up to 1964 have already been examined in a monograph[2], studies published from 1964 to 1976 are discussed in the present review.

II. THE HYDRIDE ADDITION OF ORGANOHYDROSILOXANES TO COMPOUNDS WITH A MULTIPLE CARBON–CARBON BOND

The addition of organohydrosiloxanes as well as other hydrogen-containing organosilicon compounds to unsaturated compounds can proceed with formation of α- and β-addition products. Consequently this reaction can proceed both in accordance with the Markovnikov rule (pathway *a*) and contrary to this rule, i.e. in accordance with Farmer's rule (pathway *b*):



The hydrosilylation of hex-1-ene, hex-2-ene, and hex-3-ene by 1,1,3,3-tetramethyldisiloxane has been investigated[4]. As a result of this reaction, hex-1-ene gives rise exclusively to the 1-hexyl adduct, while hex-2-ene and hex-3-ene lead to a mixture of isomers. At the same time the hexenes themselves isomerise. The hydrosilylation reaction was carried out at 100°C for several days and the addition products obtained were converted into $(CH_3)_3SiC_6H_{13}$. The proportions of the isomers in the final products are illustrated in the Table.

The content of $(CH_3)_3SiC_6H_{13}$ isomers as a function of the structure of the initial olefin.

Initial olefin	Content of $(CH_3)_3SiC_6H_{13}$ isomers, %		
	1-hexyl	2-hexyl	3-hexyl
Hex-3-ene	76	10	14
Hex-2-ene	88	7	5
Hex-1-ene	99	traces	0

The hydride addition of pentamethyldisiloxane to hex-1-ene in the presence of various catalysts (Group VIII transition metals) has been investigated[5]. It has been shown that this reaction is effectively accelerated by rhodium and platinum complexes; palladium and nickel complexes do not catalyse this reaction.

In the hydrosilylation of styrene by methylhydrosiloxanes having the general formula $(CH_3)_{3-n}HSi-[-OSi(CH_3)_3]_n$, where $n = 0-3$, in the presence of chloroplatinic acid in isopropyl alcohol (the Speier catalyst), both α- and β-addition products are formed[6]:



The fraction of β-addition products varies from 80 to 100% depending on the structure of the methylhydrosiloxanes. The tendency of methylhydrosiloxanes to form a β-adduct decreases in the following sequence as a function of the number of trimethylsiloxy-groups (n): $0 > 3 > 2 > 1$.

It has been found[7] that in the presence of the Speier catalyst, the main reaction involving the hydrosilylation of hex-2-ene by bis(trimethylsiloxy)methylsilane is accompanied by the disproportionation of the silane, i.e. the

exchange of methyl and trimethylsiloxy-groups in accordance with the mechanism

$$(CH_3)_2HSi-[-OSi(CH_3)_3]_2 \rightarrow (CH_3)_2HSiOSi(CH_3)_3 + [(CH_3)_3SiO-]_3-SiH.$$

As a result of the above hydrosilylation reaction at 138°C for 10 h with subsequent fractionation of the products, a mixture consisting of 56.6% $[(CH_3)_3SiO]_2Si(CH_3)(C_6H_{13})$, 14.5% $[(CH_3)_3SiO]_3SiH$, and 12.5% $(CH_3)_3SiOSi(CH_3)_2(C_6H_{13})$ was obtained. In addition 6.4% of $\{[(CH_3)_3SiO]_2SiCH_3\}_2O$ (the product of the oxidation of the initial silane) was also isolated.

The hydrosilylation of 3-oxapentadiene by 1,1,3,3-tetramethyldisiloxane leads to 1,1,3,3-tetramethyl-1-(3-vinyloxyethyl)disiloxane in yields up to 15%:[8]

$$CH_2=CHOCH=CH_2 + H(CH_3)_2SiOSi(CH_3)_2H \xrightarrow{H_2PtCl_6} \rightarrow H(CH_3)_2SiOSi(CH_3)_2CH_2CH_2OCH=CH_2.$$

The low yield of the adduct and the large amount of the non-distilling residue makes 1,1,3,3-tetramethyldisiloxane relatively unpromising, according to Voronkov et al.[8], as a hydrosilylating agent.

The hydrosilylation of phenylacetylene and *p*-diethynylbenzene by 1,1,3,3-tetramethyldisiloxane in the presence of chloroplatinic acid yielded phenyl-substituted 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentanes[9]:

$$[(CH_3)_2HSi]_2O + C_6H_5C\equiv CR \rightarrow (CH_3)_2Si\begin{array}{l}\diagup\\\diagdown\end{array}\!\!\begin{array}{c}C_6H_5\ R\\|\quad|\\CH-CH\\\diagdown\quad\diagup\\O\end{array}\!\!\begin{array}{l}\diagdown\\\diagup\end{array}Si(CH_3)_2\ ;$$

R = H or C_6H_5.

The hydrosilylation of phenyl-substituted acetylenes by 1,3-diethyl-1,3-dimethyl-disiloxane proceeds similarly.

It has been found[10] that certain organosiloxycycloalkanes are capable of polymerising spontaneously. The polyaddition of 1,1,3,3-tetramethyldisiloxane to phenylacetylene and *p*-diethynylbenzene in the presence of H_2PtCl_6 in THF has been reported recently[11,12]. It has been shown that this process consists of consecutive-parallel reactions and is accompanied by the appearance of branching centres:

$$C_6H_5C\equiv CR + H-Si\begin{array}{l}\diagup\\\diagdown\end{array} \rightarrow C_6H_5CH=CRSi\begin{array}{l}\diagup\\\diagdown\end{array} + C_6H_5C=CHR$$

cis-, *trans-*

$$C_6H_5CH_2-CR\left(Si\begin{array}{l}\diagup\\\diagdown\end{array}\right)_2 \quad C_6H_5-CH-CHR \quad C_6H_5C-CH_2R\ ;$$

R = H or C_6H_5.

It has been found[11] that the rate of this reaction is determined by the equation $v = K[\equiv Si-H][C_6H_5C\equiv CR][Cat]^{0.5}$ and the apparent activation energy is 11–18 kcal mole^{-1}. The addition of pyridine in amounts comparable to the amount of the catalyst inhibits this reaction, which is believed[11] to be due to the formation of inactive platinum–pyridine complexes.

The hydrosilylation of styrene, α-methylstyrene, methyl methacrylate, and allyl cyanide by dimethyl(methylhydro)cyclosiloxanes in the presence of chloroplatinic acid has been investigated[13]. It follows from ^{1}H NMR data that the product of the addition of tetramethylcyclotetrasiloxane to α-methylstyrene has the structure $[(CH_3)_2(C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2)SiO]_4$, i.e. the reaction proceeds in accordance with Farmer's rule.

The hydrosilylation of non-1-ene, α-methylstyrene, methyl methacrylate, and allylamine by heptamethylcyclotetrasiloxane as well as the hydrosilylation of methyl methacrylate by tetramethylcyclotetrasiloxane (in the presence of chloroplatinic acid as the catalyst) has been achieved[14]. Analysis of the reaction products by infrared and ^{1}H NMR spectroscopy established, that, regardless of the nature of the unsaturated compound, the addition takes place in accordance with Farmer's rule without the opening of the initial cyclotetrasiloxane fragment.

Data have been published[15] on the hydrosilylation of allyl cyanide, styrene, α-methylstyrene, and methyl acrylate by tetramethyl- and tetraethyl-cyclotetrasiloxanes in the presence of chloroplatinic acid. The addition products were studied by infared and ^{1}H NMR spectroscopy; in contrast to the data of Reikhsfel'd and Grigor'eva[13] and Borisov[14], it was observed that in all cases the addition products are mixtures of α- and β-adducts with similar boiling points.

Andrianov et al.[16] examined the hydrosilylation by pentamethyldisiloxane and bis(trimethylsiloxy)methylsilane of a number of unsaturated compounds in the presence of H_2PtCl_6: hept-1-ene, cyclohexene, styrene, indene, allyl bromide, acrylonitrile, dicyanoethylene, 2-vinylpyridine, hept-1-yne, isopropylacetylene, 2,5-dimethylhex-3-yne-2,5-diol, isoprene, 1,4-dichlorobut-2-yne, cyclopentadiene, and dichloromethylvinylsilane. It was noted that the above methyl hydrosiloxanes do not add to acrylonitrile in dicyanoethylene. Apart from H_2PtCl_6, amines and their derivatives and Pd/C were also tried as catalysts of the addition reaction. Here too the addition does not occur, which has been explained by steric hindrance. When methylhydrosiloxanes were allowed to add to cyclopentadiene, the dimerisation of the latter was observed. Allyl bromide does not add to pentamethyldisiloxane and the interaction of these compounds leads to the formation of pentamethylbromodisiloxane.

The occurrence of side reactions was observed[17] in the addition of methylhydrosiloxanes having the general formula $(CH_3)_{3-n}HSi[OSi(CH_3)_3]_n$ to β-methylallyl chloride in the presence of chloroplatinic acid:

$$\equiv Si-H + CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2Cl \rightarrow \underset{\text{(I)}}{\equiv SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl} + \underset{\text{(II)}}{\equiv SiCl} + \underset{\text{(III)}}{\equiv SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2}.$$

Depending on the structure of the initial methylhydrosiloxane, different amounts of reaction products are formed. Thus pentamethyldisiloxane forms only addition products (I) in 97% yield. Bis(trimethylsiloxy)methylsilane gives rise to 34% of (I), 18% of (II), and 9% of (III). Tris(trimethylsiloxy)silane forms the following products: 14% of (I), 42% of (II), and 23% of (III). According to the current ideas[18] about the mechanism of the hydrosilylation reaction in the presence of H_2PtCl_6, the stability of the intermediate complex with the catalyst should increase with increasing amount of the electronegative trimethylsiloxy-groups in the methylhydrosiloxane molecule; this should lead to an increase of the reactivity of the methylhydrosiloxanes, but the role of steric factors in this reaction is also important, so that the reactivity of methylhydrosiloxanes is determined by both factors. The authors suggest that chloromethylsilanes of type (II) are formed as a result of the destabilising effect of methylhydrosiloxanes on the π-allyl complex. Silylmethylallyl derivatives (III) are probably formed from the intermediate complex of the olefin, methylhydrosiloxane, and platinum.

It has been established[19] that, when methylhydrosiloxanes react with unsaturated compounds, side reactions occur together with hydrosilylation:

$$(CH_3)_3SiOSi(CH_3)_2H + CH_2=CH-CH(OCH_3)_2 \xrightarrow{H_2PtCl_6} \rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2CH_2(OCH_3)_2 + (CH_3)_3SiOSi(CH_3)_2(OCH_3) + + (CH_3)CH=CH(OCH_3) .$$

The addition of 1,1,3,3-tetramethyldisiloxane takes place similarly, the β-adducts being formed in both cases.

The addition of linear organohydrosiloxanes to allylamine has been investigated[20]. In the presence of H_2PtCl_6 or the complex of platinum with the vinylpyridine ligand $[(C_5H_5NCH=CH_2)Cl]_2Pt$ allylamine reacts with pentamethyldisiloxane and 1,3-dimethyl-1,3-diphenyldisiloxane to give at 150°C addition products containing the amino-group in the γ-position in the organic group relative to the silicon atom.

The hydrosilylation of allylamine by α,ω-bis(hydromethylsiloxy)methylphenylsiloxane leads to α,ω-bis(γ-aminopropyldimethylsiloxy)methylphenylsiloxanes[21]. On polycondensation with dicarboxylic acids of the dimethylsiloxane series, the latter give rise to elastic organosilicon polyamides, which are soluble in organic solvents.

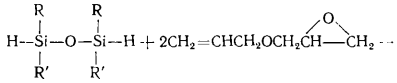
Monoaddition products have been obtained by the reaction of alkyldiallylamines $RN(CH_2CH=CH_2)$, where $R = CH_3$, C_2H_5, or n-C_4H_9, with 1,1,3,3-tetramethyldisiloxane[22]. Kinetic studies[22] have shown that 1,1,3,3-tetramethyldisilazane is less reactive than 1,1,3,3-tetramethyldisiloxane in the hydrosilylation of diallylethylamine.

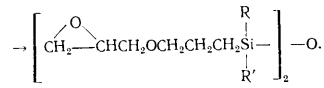
It is noteworthy that pentamethyldisiloxane and 1,1,3,3-tetramethyldisiloxane react with 2-vinylpyridine to form α-addition products only, while heptamethyl-, hexamethyl-, pentamethyl-, and tetramethyl-cyclotetrasiloxanes give rise to a mixture of α- and β-addition products under these conditions[23].

A convenient method for the synthesis of nitroaryl(alkyl)siloxanes involves the hydrosilylation of *m*-nitrostyrene by organohydrosiloxanes[24]. The reaction of 1,1,3,3-tetramethyldisiloxane and heptamethylcyclotetrasiloxane with *o*-, *m*-, and *p*-aminostyrenes in the presence of the Speier catalyst yielded the corresponding aminoaryl(alkyl)siloxanes[25]. ^1H NMR and gas–liquid chromatography (GLC) established that hydrogen and the silicon atom in methylhydrosiloxanes adds to both α- and β-carbon atoms of the C=C bond in aminostyrenes. The addition of 1,1,3,3-tetramethyldisiloxane to thienylmethylphenylvinylsilane has been achieved in the presence of the Speier catalyst[26]. Mono- and di-addition products, which are β-adducts, are formed as a result.

The corresponding organosilicon derivatives have been obtained by the addition of bis(trimethylsiloxy)methylsilane to *N*-propargylpiperidine, perhydroazepine, and morpholine in the presence of H_2PtCl_6.[27] Mono- and di-substituted acetyl- and γ-chloropropyl derivatives of disiloxane have been obtained by the hydrosilylation of vinyl acetate and allyl chloride respectively with 1,3-dimethyl-1,3-diphenyldisiloxane in the presence of H_2PtCl_6.[28]

The reaction of dihydromethylsiloxanearylenes with epoxy-compounds containing an unsaturated bond yielded organosilicon epoxy-derivatives in yields up to 80%. The reaction was carried out at 60–70°C in the presence of chloroplatinic acid[29]. Organosilicon epoxy-compounds with various substituents at the silicon atom have also been obtained by the addition of 1,1,3,3-tetraorganodisiloxanes to unsaturated epoxides in the presence of the Pt/C catalyst[30]:





It has been recommended[30] that the diaddition products be used as modifying additives to epoxy-resins and also to phenolic, alkyd, and polyester resins in order to increase their thermal stability. Following their addition to organosilicon resins, the diaddition products improve the adhesion of the former and their mechanical properties[30].

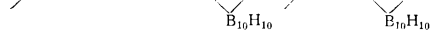
Compounds of the type

$$(CH_3)_3SiO-[-(CH_3)Si-[-(CH_2)_xO(C_2H_4O)_y-]-AO-]_n-Si(CH_3)_3,$$
$$A = H \text{ or } COOR,$$

have been obtained by the addition of methylhydrosiloxanes to polyethers containing an unsaturated group, in the presence of H_2PtCl_6. The products are recommended as additives to polyurethane foam plastics[31]. Products with an analogous structure, recommended as foam stabilisers in the manufacture of flexible polyetherpolyurethanes, have also been described in patents[32,33].

Hydrosilylation of acrylic[34,35], and methacrylic[36] acids by α,ω-dihydromethyl(methylphenyl)siloxanes in the presence of the Speier catalyst yielded the corresponding organosiloxane-α,ω-dicarboxylic acids. It has been established by infrared spectroscopy that these reactions give rise to β-addition products.

Carbaborane derivatives of silicon have been obtained by the addition of 1,3-dichlorotrimethyldisiloxane and heptamethylcyclotetrasiloxane to unsaturated carbaborane derivatives[37]:



Isopropenylcarbaborane also adds to linear polyalkylhydrosiloxanes with formation of linear polycarbaboranesiloxanes[38].

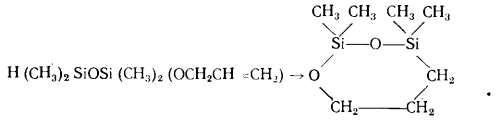
Polyorganosiloxanes containing the $\geq Si-H$ groups react with various organic compounds via the hydrosilylation mechanism[39]. It has been shown, for vinyl derivatives of styrene and divinylbenzene, that the addition of polyorganohydrosiloxanes proceeds in accordance with Farmer's rule.

The hydride addition of polyorganohydrosiloxanes to allyl acetate in the presence of platinum catalysts yielded liquids which are suitable for hydraulic shock absorbers in motor cars[40].

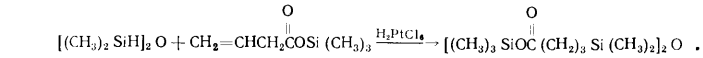
Reactions involving the hydride addition of organohydrosiloxanes to various organosilicon compounds containing unsaturated organic groups as well as the addition of hydrogen-containing organosilicon compounds to organosiloxanes with unsaturated organic substituents have been reported[2]. The addition of chloromethylhydro- and chloroethylhydro-silanes to methylvinylcyclosiloxanes has been described[41,42]. In the presence of the Speier catalyst these reactions yielded compounds capable of being converted further via their hydrolytic condensation. The addition reactions proceed with formation of β-addition products. The hydride addition of 1,1,3,3-tetramethyldisiloxane and tetramethylcyclotetrasiloxane to chloromethylvinyl- and methoxy-silanes in the presence of H_2PtCl_6 have been used to synthesise the initial compounds for the preparation of oxadisilacyclopentanes[43].

It has been shown[44] that, when allyloxyhydromethylsiloxanes are heated in the preeence of the Speier catalyst, intramolecular cyclisation takes place with formation of

methyloxasilacycloalkanes, for example:

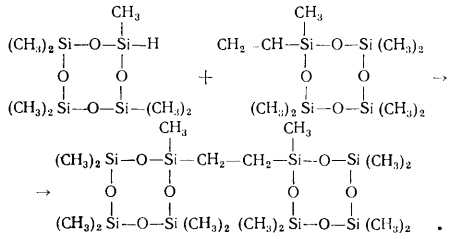


The addition of 1,1,3,3-tetramethyldisiloxane to trimethylsilyl vinylacetate has also been achieved[45]:



2-Silalactones have been obtained by the hydrolysis of the product.

A bicyclic organosiloxane has been obtained by the reaction of heptamethylvinylcyclotetrasiloxane and heptamethylcyclotetrasiloxane in the presence of chloroplatinic acid[46]:

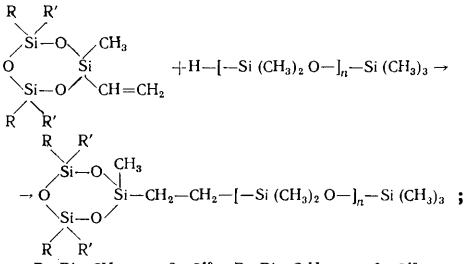


A bicyclic product of the addition of hexamethylphenylcyclotetrasiloxane to heptamethylvinylcyclotetrasiloxane has been obtained similarly[46].

The addition of pentamethyldisiloxane to heptamethylvinylcyclotetrasiloxane in the presence of various complex catalysts based on Group VIII transition metals has been investigated in detail[5,47]. The addition products were isolated by preparative GLC; analysis of the infrared and ^{1}H NMR spectra showed that, in the presence of platinum and rhodium compounds, this reaction proceeds mainly with formation of β-adducts.

The addition of pentamethyldisiloxane and 1-hydroheptamethyltrisiloxane to bis(methylphenyl)bis(methylvinyl)-cyclotetrasiloxane yielded the corresponding organocyclotetrasiloxanes containing dimethylsiloxane chains with terminal trimethylsiloxy-groups as a framework surrounding the silicon atom[48]. Infrared and ^{1}H NMR data led to the conclusion that the addition products are β-adducts. They do not polymerise under the influence of anionic catalysts [KOH at 140°C; $(CH_3)_4NOH$ at 80°C]. The addition of sulphuric acid (1%) induces structure formation in these adducts at 50°C in the course of 3 h with formation of cross-linked polymers.

The addition of vinylorganocyclotrisiloxanes to compounds having the general formula $H-[-Si(CH_3)_2O-]_n-Si(CH_3)_3$, which results in the formation of organocyclotrisiloxanes with methylsiloxane-ethylene groups at the silicon atom, has also been investigated[49,50]:



Dimethylcyclotrisiloxanes with methylsiloxane-ethylene branches give rise to cross-linked polymers in the presence of tetramethylammonium polydimethylsiloxanolate at temperatures from 20° to 75°C. This has been attributed[50] to chain transfer to siloxane-ethylene groups under the conditions of block polymerisation. Diphenylcyclotrisiloxanes with methylsiloxane-ethylene branches form polymers with a molecular weight of 187 000 under these conditions, the size of the siloxane-ethylene group in the initial compounds having little influence on the rate of formation of polymers.

Organosiloxanes with a cyclolinear structure have been obtained by the addition of pentamethyldisiloxane to hexamethyldivinylcyclotetrasiloxane in the presence of tris(triphenylphosphine)rhodium chloride[51]. It has been established with the aid of infrared and ^{1}H NMR spectroscopy that they are products of β-addition with an admixture (up to 10%) of α-addition products. GLC showed that both monoaddition and diaddition products are a mixture of stereoisomers. Cyclolinear organosiloxanes have also been obtained by the addition of α,ω-dihydrodimethylsiloxanes having the general formula $HSi(CH_3)_2O-[-Si(CH_3)_2O-]_n-Si(CH_3)_2H$ ($n = 0-3$) to heptamethylvinylcyclotetrasiloxane in the presence of tris(triphenylphosphine)rhodium chloride[52]. Analysis of the addition products with the aid of infrared and ^{1}H NMR spectroscopy established that the reaction proceeds preferentially in accordance with Farmer's rule

Reactions involving the addition of pentamethyldisiloxane to methylvinylsiloxanes having the general formula $(CH_3)_{3-n}(CH_2{=}CH)Si-[-OSi(CH_3)_3]_n$, where $n = 0-3$,[53] as well as reactions involving the addition of heptamethylvinyldisiloxane to methylhydrosiloxanes having the general formuls $(CH_3)_{3-n}HSi-[-OSi(CH_3)_3]_n$, where $n = 0-3$, have been described[54]. It has been shown that in the presence of platinum and rhodium compounds these reactions proceed with the preferential formation of β-adducts.

Organosiloxanes with ferrocene groups[55] have been obtained by the reaction of organosilicon ferrocene derivatives containing the $\geq Si-H$ bond with allylorganosiloxanes.

III. THE HYDRIDE POLYADDITION OF ORGANODIHYDROSILOXANES TO DI- AND POLYFUNCTIONAL UNSATURATED COMPOUNDS

This section deals with methods for the preparation of polycarbaorganosiloxanes using the hydride polyaddition of organohydrosiloxanes to organoalkenylsiloxanes and to organoalkenylhydrosiloxanes. Various organosilicon oligomers and polymers have been synthesised by the hydride polyaddition reaction[2,3,38]. There are two main methods for the preparation of oligomers and polymers of this kind.

1. Polyaddition of organosilicon compounds containing both an $\geq Si-H$ linkage and an unsaturated group in the molecule:

where R are various organic groups and R′ is an organic group with $n \geq 0$.

2. Polyaddition of organosilicon compounds containing two or more $\geq$Si–H linkages to bifunctional or polyfunctional unsaturated compounds (a) or to acetylene and its derivatives (b):

$$\text{a)}\quad m\,\mathrm{H}-(-\mathrm{SiR_2O}-)_n-\mathrm{SiR_2H} + m\,(\mathrm{CH_2{=}CH})_2\,\mathrm{A} \xrightarrow{\text{cat.}} \rightarrow -[(-\mathrm{SiR_2O}-)_n-\mathrm{SiR_2}\,(\mathrm{CH_2})_2\,\mathrm{A}\,(\mathrm{CH_2})_2-]_m- \quad ,$$

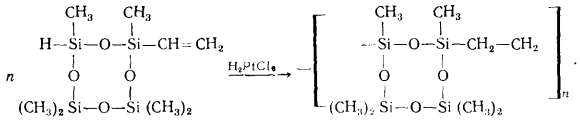
where R are various organic groups, A is an organic or organoelemental group, and $n \geq 0$;

$$\text{(b)}\quad m\,\mathrm{H}-(-\mathrm{SiR_2O}-)_n-\mathrm{SiR_2H} + m\,\mathrm{CH}{\equiv}\mathrm{CH} \xrightarrow{\text{cat.}} \rightarrow -[(-\mathrm{SiR_2O}-)_n-\mathrm{SiR_2}-\mathrm{CH_2}-\mathrm{CH_2}-]_m- \quad ,$$

where R are various organic groups and $n \geq 0$.

The possibility of synthesising linear polymeric products by the polyaddition reaction of *p*-vinylphenylmethylhydrosiloxanes having the general formula $CH_2{=}CHC_6H_4.Si(CH_3)_2-[-OSi(CH_3)_2-]_n-H$, where $n = 1-4$, has been demonstrated[56]. Polycarbaorganocyclosiloxanes have been obtained by the polyaddition of organohydrocyclotetrasiloxanes, containing vinyl and allyl groups, in the presence of H_2PtCl_6.[57,58]

The polyaddition reaction of hexamethylvinylcyclotetrasiloxane, whose polymeric products contain methylcyclotetrasiloxane units in the main chain linked by ethylene bridges, has been studied in greater detail[59]:



The reaction was carried out in carbon tetrachloride solution at 75°C in the presence of H_2PtCl_6. The products were viscous liquids with a molecular weight of 2200, which dissolved in benzene and other organic solvents. The infrared and ^{1}H NMR spectra of the addition products did not reveal the presence of the $\rangle$CH–CH$_3$ group, which led the authors[59] to the conclusion that the polyaddition reaction takes place with formation of β-adducts. Kinetic measurements at 50–80°C and a catalyst concentration of $(1.4-4.2)\times10^{-4}$ mole/mole showed that the reaction is described satisfactorily by a second order equation with respect to the monomer with first-order control with respect to the catalyst. It was shown that the reaction proceeds via a state involving the formation of an intermediate compound of the monomer and the catalyst.

Methods have been developed for the synthesis of polycarbaorganosiloxanes by the polyaddition of dihydroorganosiloxanes to dialkenylorganosiloxanes. This work was initiated by a study[60] of the addition of 1,3-diethyl-1,3-dimethyldisiloxane to 1,3-diethyl-1,3-dimethyl-1,3-divinyldisiloxane and to 1,3-diallyl-1,1,3,3-tetramethyldisiloxane in the presence of H_2PtCl_6. Next mention should be made of studies involving the polyaddition of α,ω-dihydrodimethylsiloxanes to α,ω-divinyl- and α,ω-diallyldimethylsiloxanes in the presence of Pt/C.[56,61] The products were linear polymers having the general formula

$$\mathrm{R(CH_3)_2Si}-\{[-\mathrm{OSi(CH_3)_2}-]_n-(\mathrm{CH_2})_m-\}_x-\mathrm{Si(CH_3)_2}-[-\mathrm{OSi(CH_3)_2}-]_n-\mathrm{R'};$$

R=R′=—CH=CH$_2$ or H, m=2, n=2, 4, 5, x=3–250;

R=R′=—CH$_2$—CH=CH$_2$ or H, m=3, n=1, 2, x=3–250.

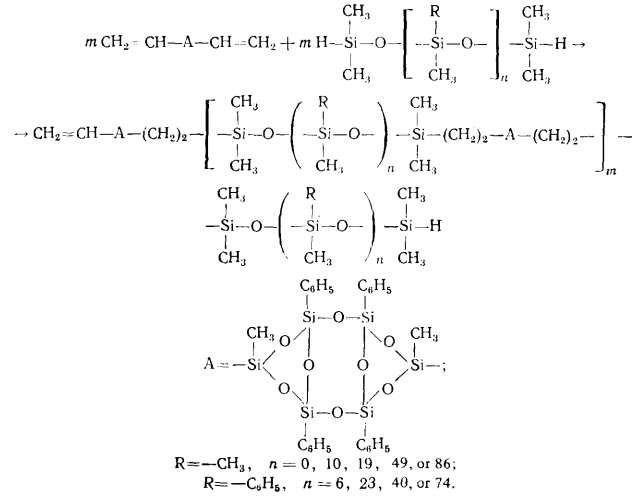
Their molecular weights, determined cryoscopically and on the basis of the content of the end groups, were 1000 to 25 000. The polyaddition products consisted of viscous liquids or gel-like substances. Infrared spectra led to the conclusion[56,61] that these are β-polyaddition products without $\rangle$CH–CH$_3$ groups.

The polyaddition of linear dihydromethylsiloxanes to methyldivinylsiloxanes with terminal trimethylsiloxy-groups has been studied in the presence of the Speier catalyst[62]. Products with a molecular weight <2000, consisting of slightly viscous liquids, were obtained. Comparison of the rates of addition of $[(CH_3)_2SiH]_2O$ and $(CH_3)_3SiO-[-(CH_3)HSiO-]_2-Si(CH_3)_3$ to $(CH_3)_3SiO-[-(CH_3).(CH_2{=}CH)SiO-]_2-Si(CH_3)_3$ established that 1,1,3,3-tetramethyldisiloxane adds 100 times faster than methyldisiloxane with terminal trimethylsiloxy-groups. The difference between the rates of addition is attributed to steric hindrance. It has been shown by ^{1}H NMR that β-addition products are formed.

The polyaddition of α,ω-dihydro-organosiloxanes to α,ω-divinylorganosiloxanes with methyl, ethyl, and phenyl groups at the silicon atoms has also been studied[63]. It was established that, for both α,ω-divinylorganosiloxanes and α,ω-dihydro-organosiloxanes, the rate of reaction decreases when the methyl group is replaced by the more electronegative phenyl group. Together with electronic factors, the rate of reaction is influenced also by steric factors.

Linear polycarbadiorganosiloxanes with methylcyclotetrasiloxane fragments in the polymer chain have been obtained by the polyaddition of α,ω-dihydrodimethylsiloxanes to hexamethyldivinylcyclotetrasiloxane[64]. The polyaddition reaction was carried out in an atmosphere of argon with an equimolar ratio of the initial components at 100–110°C for 50–160 h. The catalyst was chloroplatinic acid in an amount of $(1-1.5)\times10^{-5}$ g per gramme of the initial mixture. Part of the catalyst was introduced before the start of the reaction and the rest after 25–140 h. The products were viscous colourless transparent liquids whose molecular weight increased from 75 000 to 471 000, depending on the molecular weight of the initial α,ω-dihydrodimethylsiloxane. When the addition products were heated in the presence of 0.0001–0.1% of an anionic polymerisation catalyst, the viscosity increased sharply and a gel was formed.

Polyorganosiloxanes with linear and cyclic fragments in the chain have been obtained[65] by the addition of 1,7-dimethyl-3,5,9,11-tetraphenyl-1,7-divinyltricyclohexasiloxane to α,ω-dihydrodimethyl(methylphenyl)-siloxanes in the presence of H_2PtCl_6 in THF:



Polymers with linear dimethylsiloxane and aromatic fragments in the chain have been synthesised by the addition of diallyl isophthalate to α,ω-dihydrodimethylsiloxanes[65]. It was established[65] that, with increase of

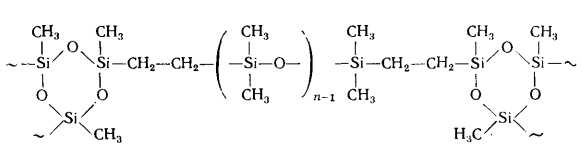
the fraction of siloxane tricyclic and aromatic fragments in the linear siloxane chain, the glass points of the polymers increase. Thermogravimetric analysis showed that the stability of the polymers in relation to thermo-oxidative degradation increases with increasing fraction of aromatic fragments in the linear dimethylsiloxane chain.

Three-dimensional polymers have been obtained by the polyaddition of tetramethylcyclotetrasiloxane to tetramethyltetravinylcyclotetrasiloxane in the presence of chloroplatinic acid[66], while polyaddition of α,ω-dihydrodimethylsiloxanes having the general formula $H(CH_3)_2SiO-[-Si(CH_3)_2O-]_n-Si(CH_3)_2H$, where $n = 0-200$, to tetramethyltetravinylcyclotetrasiloxane yielded cross-linked polycarbadiorganosiloxanes with a regular structure[67]. In the latter case the polyaddition reaction was carried out at 100–110°C in the presence of H_2PtCl_6. Depending on the ratio of the initial components, liquid or solid, infusible products, partly soluble in organic solvents, were obtained. The study of the properties of the products established that their thermo-oxidative stability decreases with increasing length of linear organosiloxane units. The authors explain[67] this phenomenon by the fact that, when the products are heated above 200°C, the rings in the polymer structure apparently open with a consequent increase in network density. This process results in an inhibition of degradation. The relatively low temperature of the onset of thermo-oxidative degradation of polymers, which is 310°C for $n = 0$ in the initial α,ω-dihydrodimethylsiloxane or 200°C for $n = 200$, is attributed to the presence of the platinum catalyst in the products.

The mechanical properties of cross-linked organosilicon polymers obtained by the polyaddition of 1,5-dihydrohexamethyltricyclosiloxane to trimethyltrivinylcyclotrisiloxane and to tetramethyltetravinylcyclotetrasiloxane have been investigated[68]. The existence of structural formations, which decompose as a result of slight deformations and under the influence of temperature, was noted.

Polymers have been synthesised by the addition of tetramethylcyclotetrasiloxane to trimethyltrivinylcyclotrisiloxane, to tetramethyltetravinylcyclotetrasiloxane, and to tetraphenyltetravinylcyclotetrasiloxane in the presence of H_2PtCl_6.[69] Thermogravimetric analysis of the products in oxidising (in air) and inert (in a stream of argon) atmospheres showed that the thermal and thermo-oxidative stabilities of the polymers, determined by the temperature of the onset of decomposition of the polymer in the course of dynamic heating, are independent of the nature of the groups surrounding the silicon atom. However, the temperature at which 10% of the weight of the polymer is lost depends on the nature of the organic groups at the silicon atom in both inert and oxidising atmospheres. For polymers with methyl groups, this temperature is higher than for polymers with phenyl groups.

The influence of the crystallisation of cross-linked polycarbadimethylsiloxanes with rings at the nodes of the network, of the type



$n = 36, 60, 150$,

on longitudinal NMR relaxation has been investigated[70]; it was shown that, with increase of the extent of the linear dimethylsiloxane chains, i.e. in the sequence $n = 36$, 60, 150, the segmental mobility of the chains between the network nodes increases.

It follows from the foregoing that the hydride addition of organohydrosiloxanes to organoalkenylsiloxanes is widely used to synthesise a wide variety of monomers, oligomers, and polymers. The reaction is also used for the hardening of organosilicon resins, the vulcanisation of siloxane elastomers, and the synthesis of various compositions.

The preparation of cross-linked polymers by the addition of polyhydro-organosiloxanes to polyvinylorganosiloxanes has been studied[71,72] in the presence of H_2PtCl_6 and it has been established that the replacement of methyl groups by phenyl groups in the initial polyorganosiloxanes leads to a decrease of the degree of hardening of the products due to steric hindrance, which interferes with the polyaddition reaction. Compared with their polyorganosiloxane analogues, polymers with disilylethylene groups exhibit a smaller thermo-oxidative stability but a greater thermal stability under conditions which rule out the dissociation of the C–C bond as a result of oxidation, i.e. in the absence of atmospheric oxygen[71,72].

The vulcanisation of linear polyorganosiloxanes with vinylsiloxy-units in the chain has been achieved by the hydride addition reaction; various organohydrosiloxanes were then used as structure-forming agents[73]. The vulcanisation was as a rule carried out at 50–100°C, which led to the formation of disilylethylene groups, which then functioned as cross-linking units in the formation of linear diorganosiloxane macromolecules. The use of polyorganosiloxanes containing vinyl groups makes it possible to obtain polymeric coatings with an enhanced strength and flexibility[74]. Elastic compositions suitable as adhesives and current-conducting materials have been obtained on the basis of the above cross-linking agents[75] using various hydrosilylation catalysts, in the first place H_2PtCl_6 and platinum complexes[74,76].

Polyorganosiloxanes which are effective foam stabilisers for the preparation of fire resistant polyurethane foam plastics have been synthesised by hydride addition in the presence of the above catalysts[77].

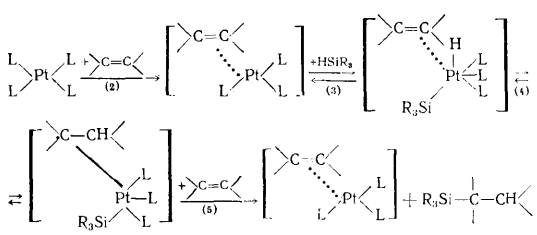
IV. THE PRINCIPAL FACTORS INFLUENCING THE COURSE OF THE HYDRIDE ADDITION REACTION

The addition of organohydrosiloxane to organovinylsiloxanes is a special case of the hydride addition reaction and obeys the general rules governing the latter. The hydride addition reaction is influenced, together with general factors (concentrations of the reactants, reaction temperature and time, the nature of the solvent, etc.), also by specific factors such as the type of catalyst used and the structure of the unsaturated and hydrogen-containing organosilicon compounds. This section deals with the effects of such specific factors.

The hydride addition reaction can be carried out in the absence of catalysts; for example, the addition of trichlorosilane to olefins at 300°C takes place without a catalyst[78,79]. Various initiators and hydride addition catalysts are used to reduce the temperature, to increase the rate of reaction, to increase the yield of addition products, and to suppress undesirable side reactions. The initiating effect of ultraviolet light, γ-radiation, various peroxy-compounds and other substances readily forming free radicals, as well as organic electron-donating compounds such as amines, amides, phosphines has been demonstrated[2,3].

Group VIII metals fixed on carriers or forming part of the composition of various compounds are effective catalysts of the hydride addition reaction. Compounds of other metals (copper, zinc, zirconium, chromium, molybdenum, etc.) are also known to exhibit a catalytic activity. The most active catalyst is chloroplatinic acid[80], which is used in the form of a solution in isopropyl alcohol (the so-called Speier catalyst). By virtue of the ease of its use and high catalytic effect, chloroplatinic acid is the most common catalyst of reactions of this type. However, its application also suffers from certain disadvantages, namely an induction period necessary for the manifestation of catalytic action, in some cases an acceleration of side reactions, and insolubility of the catalyst in many organic solvents.

On the basis of detailed studies of hydride addition[18] and by analogy with other homogeneous-catalytic processes, a mechanism has been proposed for the hydride addition reaction catalysed by H_2PtCl_6,[81] the first stage of which involves the formation of a platinum complex $Pt(L)_4$ with replacement of chlorine atoms by hydrogen; R_3SiH is the source of hydrogen. Next the reaction proceeds in accordance with the following scheme:

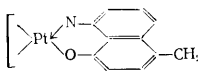


where L = Cl, H, or a coordinated solvent molecule.

Thus the hydride addition reaction consists of the following stages: (1) reduction of H_2PtCl_6 by the organosilicon hydride; (2) π-coordination of the unsaturated component with simultaneous displacement of one of the ligands; (3) oxidative addition of the organosilicon hydride with formation of an unstable hexacoordinate platinum complex with inclusion in the inner sphere of hydrogen and the silyl group; (4) displacement of a hydrogen atom from platinum to the coordinated olefin and the formation of an alkyl–platinum σ bond; (5) reductive displacement of the alkylsilane via the coordination of another molecule of the unsaturated component.

The catalytic effect of Group VIII transition metal complexes has been recently examined in many studies of the hydride addition reactions. The use of complexes of various metals in different oxidation states and coordinated to a wide variety of ligands as catalysts has been described. On the basis of the mechanism proposed above, which has been extended[18] to Group VIII transition metal complexes, a distinct catalytic effect is to be expected for compounds which satisfy the following requirements: (a) unsaturated reagents can coordinate to them; (b) they activate the hydrogen-containing organosilicon reagent, i.e. they cleave the $\geq$Si–H bond and at the same time both fragments formed can be coordinated to them; (c) they are not reduced by hydrogen-containing organosilicon compounds with formation of the free metal.

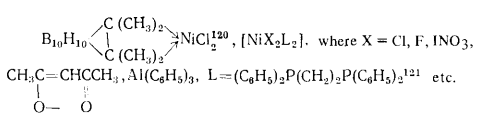
The following platinum complexes can be used as catalysts of the hydrosilylation reaction: $\{[(C_6H_5)_3P]_2.Pt(C_2H_4)\}$[82] and $[(C_6H_5)_3P]_4Pt$[83–85]—i.e. compounds containing zerovalent platinum; $(alkene)_2PtCl_2$,[86–88] $[(C_6H_5)_3P]_2PtCl_2$,[89] $(CH_3CN)_2PtCl_2$ and $(C_6H_5CN)_2PtCl_2$,[90] *trans*-$[(C_2H_5)_2OSC_2]_2.PtCl_2$,[91] *cis*-$(CO)_2PtCl_2$,[92] $[(CH_3)_3Si(CH_2)_nP(C_4H_9)_2]_2PtCl_2$ with $n = 1-3$,[93] $(cyclo\text{-}C_6H_{11})_2PtCl_2$,[94] and di-iodohexamethyldipyridineplatinum[95]—i.e. compounds containing bivalent platinum; $[Pt(CH_3)_3]_2$ and $(CH_3)_3PtI$[96]—i.e. compounds containing quadrivalent platinum; the polymeric chelate complex[97]



complexes of platinum chlorides with olefins, compounds of the pyridine series, thioimides, alkylthioureas, phosphines, and nitriles[98], platinum complexes with olefins or cyclopropane[99], as well as platinum complexes stabilised by phosphines and nitriles[100].

Palladium complexes have also recently begun to be used as catalysts of the hydride addition reaction, although they are readily reduced by the hydrogen-containing compounds. The complexes $[(C_6H_5)_3P]_4Pd$,[101,102] metallic palladium, and bivalent palladium complexes with ligands such as trialkyl(aryl)phosphines[101], $Pd(PR_3)_mL_n$, where R is an aliphatic, aromatic or alicyclic group, L is another ligand or an acid residue, $m = 1-4$, and $n + m = 4$,[103] nitrile complexes of bivalent palladium halides[104,105], $(R_3P)_2PdCl_2$,[106] $[(CH_3)_3SiCH_2P.(C_4H_9)_2]_2PdCl_2$,[93] a polymeric chelate complex containing palladium[97], the complex $[PdCl(\pi\text{-}C_5H_5)_2]$,[107] and other palladium complexes also exhibit effective catalytic properties.

A catalytic activity in hydrosilylation reactions has been noted for certain nickel complexes. In particular, nickel carbonyl compounds $Ni(CO)_4$[108] and $[(\pi\text{-}C_5H_5)_2Ni(CO)]_2$,[109] phosphine complexes of nickel $(R_3P)_2NCl_2$ and $\{[C_6H_5)_3P]_2Ni(C_2H_4)\}$,[110–112] $(C_5H_5N)_2NiCl_2$, $Ni(Cp)_2$, and $\{[(C_6H_5)_3P]Ni(Cp)(C_2H_5)\}$, where Cp is the cyclopentadienyl ligand[113], $Ni(acac)_2 + Al(C_2H_5)_3$,[114–118] $Ni(COD)_2$ and the $NiCl_2$ (or $NiBr_2$) + PR_3 + sodium bis-(2-methoxyethoxy)-hydroaluminate[119], a polymeric chelate complex (whose structure is analogous to that of the chelate complex of platinum mentioned above)[97], the complexes $[(CH_3)_3Si.(CH_2)_nPR_2]_2NiX_2$, where $n = 1$ or 2, R = C_4H_9 or C_6H_5, and X = Cl or Br,[93] and



It is believed[122] that the mechanism of the addition of organohydrochlorosilanes to olefins in the presence of phosphine complexes of nickel is analogous to the mechanism of the hydrosilylation reaction in the presence of H_2PtCl_6. The hydrosilylation reaction in the presence of phosphine complexes of nickel takes place at a temperature $>90°C$ and most effectively at ~120°C.[122] It is accompanied by the exchange of hydrogen and chlorine atoms:

$$2RCH{=}CH_2 + 3R'_2SiHCl \xrightarrow{Ni^{II}} RCH_2CH_2SiR'_2Cl + RCH_2CH_2SiR'_2H + R'_2SiCl_2.$$

The exchange is faster and more extensive the more pronounced are the electro-accepting properties of the phosphorus-containing ligands. It has been found[122] that the addition takes place *cis*-stereospecifically. As in catalysis by H_2PtCl_6, the reactivities of chloromethylhydrosilanes decrease in the sequence

$$HSiCl_3 > (CH_3)\,HSiCl_2 > (CH_3)_2\,HSiCl \gg HSi\,(CH_3)_3.$$

It is of interest that the catalytic action of nickel(II) complexes is characterised by a longer induction period than the action of the zerovalent complexes. Among

cobalt complexes, the carbonyl compounds have been widely used as catalysts of the hydrosilylation reaction. These are primarily dicobalt octacarbonyl and π-cyclopentadienyldicobalt dicarbonyl[123], in the presence of which the hydrosilylation reaction sometimes takes place even at room temperature.

It has been established[124] that, in the presence of dicobalt octacarbonyl, the addition of $\geq$Si–H to olefins is directed to form β-adducts, this being accompanied by the isomerisation of the initial olefin. In view of the low thermal stability of dicobalt octacarbonyl, when the reaction is carried out at a temperature >60°C, the yield of addition product falls. It is believed[125] that the reaction includes the following stages:

$$R_3SiH + Co_2(CO)_8 \rightarrow R_3SiCo(CO)_4 + HCo(CO)_4 ,$$

$$HCo(CO)_4 + R'CH=CH_2 \rightarrow R'CH_2CH_2Co(CO)_4 ,$$

$$R'CH_2CH_2Co(CO)_4 + R_3SiH \rightarrow R'CH_2CH_2SiR_3 + HCo(CO)_4 ,$$

$$R'CH_2CH_2Co(CO)_4 + R_3SiCo(CO)_4 \rightarrow R'CH_2CH_2SiR_3 + Co_2(CO)_8 .$$

There is also a possibility of the reactions

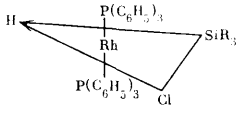
$$2HCo(CO)_4 \rightarrow Co_2(CO)_8 + H_2 ,$$
$$HCo(CO)_4 + R_3SiH \rightarrow R_3SiCo(CO)_4 + H_2 .$$

The latter are undesirable and so is the formation of the complex $R_3SiCo(CO)_4$, which is catalytically inactive. An excess of the unsaturated compound is necessary to suppress these undesirable reactions.

The hydrosilylation reaction has been achieved in the presence of the phosphine complexes of cobalt $[(C_6H_5)_3P]\cdot CoH_3$, $[(C_6H_5)_3P]CoH(N)$,[126] a two-component system of the Ziegler type $Co(acac)_2 + Al(C_2H_5)_3$,[115-118] etc.

Rhodium complexes are highly active as catalysts of the hydrosilylation reaction. These are primarily the phosphine complexes $[(C_6H_5)_3P]_3RhCl$ (the so-called Wilkinson catalyst),[127-129], $[(C_6H_5)_2PH]_3RhCl$,[130] $\{[(C_6H_5)_3P]_4RhH\}$,[131] $\{[Rh(1,5\text{-}C_6H_{12})Cl]_2\} + L$, where L = P(cyclo-$C_6H_{11})_3$, $P(CH_3)_2C_6H_5$, $PCH_3(C_6H_5)_2$, $P(C_6H_5)_3$, $P(OC_4H_9\text{-}n)_3$, $P(OC_6H_5)_3$, or $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$,[132] $\{L_2RhH[Si(OC_2H_5)_3]Cl\}$, where L = $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)\cdot(C_6H_5)_2P$, C_6H_5 (cyclo-$C_6H_{11})_2P$, or $(C_6H_5)_2$(cyclo-$C_6H_{11})P$,[133] the carbonyl complexes $[(CO)_4Rh_2Cl_2]$,[125] $\{[(C_6H_5)_3P]_2\cdot Rh(CO)Cl\}$, and $\{[(C_6H_5)_3P]_3RhH(CO)\}$,[85,125,132] the olefin complex $[(C_2H_4)_2Rh_2Cl_2]$, a polymeric chelate complex containing rhodium[97], and others.

The same mechanism, in principle, has been proposed for the hydrosilylation reaction in the presence of rhodium complexes as in the presence of H_2PtCl_6.[18] The pentacoordinate rhodium complex[127]



is believed to be catalytically active[127]. This complex is formed as a result of the reaction

$$[(C_6H_5)_3P]_3RhCl + R_3SiH \rightleftarrows [(C_6H_5)_3P]_2Rh(SiR_3)HCl + (C_6H_5)_3P.$$

Its stability under the conditions obtaining in the reactions of chloroethylhydrosilanes depends on the nature of the groups SiR_3 and decreases in the sequence

$$-Si(C_2H_5)_3 < -SiCl(C_2H_5)_2 < -SiCl_2(C_2H_5) < -SiCl_3.$$

Among other transition metal complexes proposed as catalysts of the hydrosilylation reaction, mention should be made of iron carbonyls[135], a two-component catalyst of the Ziegler–Natta type $Fe(acac)_2 + Al(C_2H_5)_3$,[115] manganese[136,137], ruthenium[138], and iridium[127] complexes, and $Co(CO)_6$ (the last complex is used in combination with ultraviolet irradiation)[139].

Together with the homogeneous catalysts indicated above, which are used in the form of solutions, catalysts based on transition metals bound to carriers have been developed recently. These forms of catalysts are interesting because they combine the advantages of homogeneous and heterogeneous catalysts, namely high catalytic activity, the possibility of the repeated use of the catalyst, and applicability to continuous processes. Thus the preparation of phosphine complexes of rhodium chemically bound to organic polymeric materials, for example, on a butadiene–styrene copolymer, and their application in hydrosilylation reactions have been described[140]. The catalyst $[Rh(CO)_2Cl]_2$ deposited on a modified styrene–divinylbenzene copolymer has also been proposed[141]. Alumina, glass, molecular sieves, silica, and other materials are also employed as catalyst carriers[140,142].

Platinised ion-exchange resins can be used as catalysts of the hydrosilylation reaction[143,144].

The catalytic activities of various platinum, rhodium, palladium, nickel, and cobalt compounds in reactions involving the addition of pentamethyldisiloxane to methylvinylsiloxanes with linear and cyclic structures have been investigated[5,145]. The palladium and nickel compounds hardly catalyse the above reactions, while the platinum and rhodium compounds exhibit a high catalytic activity. It was noted that the rhodium compounds ensure a greater β-selectivity of the addition process. Dicobalt octacarbonyl exhibits a high catalytic activity at higher concentrations.

The structure of unsaturated and hydrogen-containing organosilicon compounds exerts an appreciable influence on the rate and direction of the hydrosilylation reaction. The relative rate constants for the addition of trichlorosilane to various unsaturated compounds have been determined by the method of competition kinetics[146]. It was established that the reactivity of the unsaturated compounds depends mainly on the electron density at the double bond and sometimes on steric factors. The reactivities of the test compounds in the reaction under consideration decrease in the sequence hept-1-ene > *cis*-hept-2-ene > allylbenzene > t-butylethylene > dec-1-ene > styrene > allyl chloride > cyclohexene.

The reactivity of unsaturated compounds in relation to alkylhydrocyclosiloxanes decreases in the sequence[147] styrene > α-methylstyrene > methyl methacrylate > allyl cyanide. The decrease is correlated with the decrease of the electron density of the double bond. α-Methylstyrene, where the influence of steric factors is significant, constitutes an exception.

The rate of hydrosilylation of halogeno-olefins decreases in the following sequence in the presence of H_2PtCl_6:[148]

$$CH_2=CH_2 > CH_2=CF_2 > CF_2=CFCl > CF_2=CF_2.$$

Attack by the olefin on the $\geq$Si–H bond is easier the greater the electron density in the double bond[149]. Hydrogenation of the unsaturated component is facilitated simultaneously.

The reactivity of methylvinylsiloxanes having the general formula $(CH_2=CH)(CH_3)_{3-n}Si[OSi(CH_3)_3]_n$ decreases with increase of the number of trimethylsiloxy-groups (n was varied from 3 to 1) when sulphur compounds are added to them in the presence of H_2PtCl_6.[18]

The reactivity of methylvinylsiloxanes having the general formula $(CH_3)_{3-n}(CH_2{=}CH)Si[OSi(CH_3)_3]_n$, where $n = 0-3$, in relation to pentamethyldisiloxane in the presence of tris(triphenylphosphine)rhodium chloride has been investigated by the method of competition kinetics[53]. It was established that, with increase of the number of trimethylsiloxy-groups in methylvinylsiloxanes, the reactivity of the latter decreases in the sequence[53]

$$(CH_3)_3(CH_2{=}CH)Si > (CH_3)_2(CH_2{=}CH)SiOSi(CH_3)_3 > CH_3(CH_2{=}CH)Si[OSi(CH_3)_3]_2 > CH_2{=}CHSi[OSi(CH_3)_3]_3.$$

The influence of substituents at the silicon atom bound to the vinyl group on the reactivity of linear α,ω-divinyldiorganosiloxanes in the addition reactions of α,ω-dihydrodiorganosiloxanes has been investigated[63]. The observed rate constants for the addition reaction show that the replacement of the methyl group by the more electronegative phenyl group reduces the reactivity of vinylorganosiloxanes. The steric influence of the phenyl groups has also been noted in isolated instances.

Thus the reactivity of unsaturated compounds is higher the greater the electron density in the double bond. Naturally, in the presence of steric hindrance due to bulky substituents, the reactivity of unsaturated compounds can decrease.

The reactivity of hydrogen-containing organosilicon compounds in reactions involving addition to unsaturated compounds also depends on structural factors. Thus the reactivity of chloroethylhydrosilanes in reactions involving addition to hept-1-ene in the presence of H_2PtCl_6 increases in the following sequence[150]:

$$(C_2H_5)_3SiH < (C_2H_5)_2SiHCl < C_2H_5SiHCl_2 < HSiCl_3.$$

The observed increase of the reactivity of chloroethylhydrosilanes is due to the decrease of the electron density in the $\rangle Si-H$ bond when ethyl groups are replaced by the electronegative chlorine atoms. A similar behaviour has been observed in the study of the addition of chloroethylhydrosilanes to hept-1-ene in the presence of dicobalt octacarbonyl[151].

In the addition of hydrogen-containing organosilicon compounds to diethyl allylmalonate in the presence of H_2PtCl_6 the amount of adduct formed increases with increase of the number of electronegative substituents at the silicon atom[152]:

$$R_3SiH < R_2SiHCl < RSiHCl_2 < HSiCl_3;$$
$$R_3SiH < R_2SiH(OR') < RSiH(OR')_2 < HSi(OR')_3.$$

The reactivity of organochlorosilanes in relation to acrylonitrile decreases in the sequence[153]

$$HSiCl_3 > (C_6H_5)HSiCl_2 > (CH_3)HSiCl_2 > (C_6H_5)_2HSiCl > (C_6H_5)(CH_3)SiHCl \gg (CH_3)_2HSiCl.$$

Comparison of the relative rate constants for the addition of ethoxypropylhydrosilanes $(C_3H_7)_nHSi(OC_2H_5)_{3-n}$ to hex-1-ene in the presence of tris-(triphenylphosphine)-rhodium chloride and dicobalt octacarbonyl (determined by the method of competition kinetics) shows that the observed increase of the reactivity of ethoxypropylhydrosilanes with increasing content of ethoxy-groups takes place in the following sequence: tripropylsilane < ethoxydipropylsilane < diethoxypropylsilane < triethoxysilane[151].

There are relatively few data concerning the influence of the structure of organohydrosiloxanes on their reactivity in reactions involving addition to unsaturated compounds. The study of the kinetics of the addition of 1,1,3,3-tetramethyldisiloxane and octamethyl-3,5-dihydrotetrasiloxane to heptamethyl-3-vinyltrisiloxane showed that the introduction of the trimethylsiloxy-group into methylhydrosiloxanes hinders the reaction appreciably[62].

The reactivity of methylhydrosiloxanes having the general formula $(CH_3)_{3-n}HSi[OSi(CH_3)_3]_n$, where $n = 1-3$, in the reaction involving addition to hex-1-ene and heptamethylvinylcyclotetrasiloxane in the presence of H_2PtCl_6 is determined predominantly by steric factors[51,145]. The methylhydrosiloxanes investigated can be arranged in the following sequence in terms of the decrease of their reactivity in the above hydride addition reactions:

$$(CH_3)_2HSiOSi(CH_3)_3 > (CH_3)HSi[OSi(CH_3)_3]_2 > HSi[OSi(CH_3)_3]_3.$$

It has been established by the method of competition kinetics[52] that the reactivities of dimethyl-α,ω-dihydrosiloxanes having the general formula $H-Si(CH_3)_2O-.[-Si(CH_3)_2O-]_n-Si(CH_3)_2-H$, where $n = 0-3$, in reactions involving addition to hept-1-ene in the presence of tris-(triphenylphosphine)rhodium chloride decrease with increase of molecular weight. This can be accounted for by the decrease of molecular mobility and probably by differences in the stability of the intermediate compound involving the catalyst.

It has also been shown[52] that the replacement of the methyl group in dimethyl-α,ω-dihydrosiloxanes by the electronegative phenyl group does not increase the reactivity in reactions involving addition to methylvinylsiloxanes. The reactivity actually decreases owing to steric hindrance.

Thus the reactivity of hydrogen-containing organosilicon compounds in reactions involving addition to unsaturated compounds is determined by steric and electronic factors. In particular, the introduction of electronegative groups and the associated increase of the positive charge on the silicon atom promote the dissociation of the hydrogen atom as a proton. This is manifested by an increase of the reactivity of hydrogen-containing organosilicon compounds.

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The data reviewed show that there have been many studies on the hydrosilylation of unsaturated organic compounds and on the hydride addition of organohydrosiloxanes to organosilicon compounds containing multiple carbon–carbon bonds. It has been established that the hydrosilylation reaction is important for the synthesis of a wide variety of organosilicon compounds. Hydride addition constitutes a convenient method for the synthesis of high-molecular-weight compounds and gives rise to extensive possibilities for their modification in order to convert them into systems with three-dimensional and cross-linked structures.

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The Conformation of γ-Aminobutyric Acid and Its Analogues

I.A.Sytinskii and A.T.Soldatenkov

Theoretical and experimental data on the steric structure of γ-aminobutyric acid and its analogues are presented. The possible relation between the structural flexibility of the γ-aminobutyric acid molecule and its biological activity is examined. The bibliography includes 90 references.

CONTENTS

I. Introduction 669
II. The steric structure of γ-aminobutyric acid and its analogues 669
III. Modelling of the interaction of γ-aminobutyric acid with its receptor 675

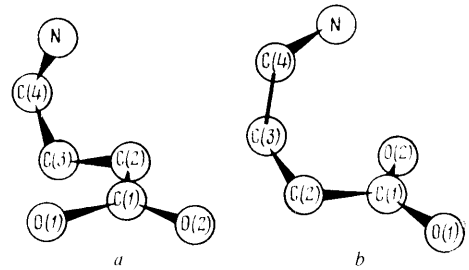
I. INTRODUCTION

γ-Aminobutyric acid (GABA) was obtained for the first time in 1883.[1] In the middle of the present century it was detected in the nerve tissues of the central nervous system (CNS) of mammals. It has recently come to be realised that GABA is one of the most important natural products from the biological point of view. It is a specific chemical mediator (transferring agent) in the inhibition of nerve pulses in CNS.[2-6] Recently (since 1960) GABA and its derivatives have begun to be used as medicinal preparations in the treatment of nervous and psychiatric conditions[7]. The successful use of GABA and its derivatives in the treatment of various neurotic and psychopathic states led to the possibility of synthesising new synthetic drugs with selective action and with a low toxicity by virtue of their similarity to the metabolic products in the brain. In this connection the problem of the influence of the steric structure of GABA on its biological and pharmacological activity assumes considerable importance. Like many substances with pharmacological activity, GABA has a non-planar structure. Conformational changes in the GABA molecule can lead to its incomplete interaction with its receptor. Probably only a specific conformation of the GABA molecule ensures the optimum disposition of its structural elements relative to the receptor, necessary for the manifestation of the maximum physiological activity. Probably not only the conformation but also the electronic properties of the molecules play a significant role in the pharmacological properties of GABA and its derivatives. Numerous studies, published during the last five years, have been devoted to the relation and between these properties and their mutual influence and to the determination of the active conformations of GABA and its analogues. Both theoretical and experimental methods are widely used in the solution of these problems.

II. THE STERIC STRUCTURE OF γ-AMINOBUTYRIC ACID AND ITS ANALOGUES

1. Quantum-Chemical Modelling of the GABA Molecule

Quantum mechanics permits an approximate calculation of the energy of molecules in terms of the molecular orbital theory by solving the Schrödinger wave equation. Since all the valence electrons can be taken into account in such calculations, the total energy of the molecule becomes sensitive to changes in its conformation. Minimisation of the total energy as a function of specified angles between bonds in the molecule makes it possible to predict its preferred energetically most favourable conformation. Quantum-chemical calculations also permit the determination of the electronic structures of the conformers from the corresponding wave functions, to predict the chemical behaviour of the molecule, to derive parameters associated with the reactivity of a biologically active molecule, etc.



a *b*

Figure 1. The skeleton of the GABA molecule: *a*) extended structure; *b*) folded structure.

Several semiempirical molecular orbital methods have been used to determine the preferred conformation of GABA.[8-10] The latter was first determined theoretically in 1970;[11] the authors carried out a calculation on this molecule with the aid of the extended Hückel method (EHM).[12] The method takes into account the interactions not only between atoms linked to one another but also between remote atoms, so that the total energy of the molecule is evaluated as a function of the coordinates of all the atoms in the molecule. The calculation showed that in the preferred conformation of GABA the 'onium and α-methylene groups are in the transoid positions and the carboxy-group can rotate freely by 360° (Fig. 1*a*). The GABA molecule is represented as a zwitterion with a distance between the charge centres (N^+ and O^-) of 5.0–6.0 Å, which corresponds to an extended (unfolded) conformation of GABA. However, one should bear in mind that the mutual repulsion of electrons is not taken into account in

EHM, so that the results can sometimes conflict with data derived by other methods, particularly for polar molecules [13].

A more exact quantum-chemical theory—the method of complete neglect of differential overlap (CNDO)—was developed by Pople [14,15]. Calculation for the GABA molecule by this method [10] led to the opposite results—a folded conformation (Fig. 1*b*) is preferred for the isolated GABA molecule in both neutral and zwitterionic forms, which is consistent with data obtained by ^1H nuclear magnetic resonance [16,17]. It has been noted [10] that the influence of the solvent can induce conformational changes and calculations have indeed demonstrated that in the presence of a solvent the extended conformation becomes preferred. However, Pople's theory also suffers from definite limitations [13]. Thus a satisfactory description of the charge distribution is obtained in most cases only for mobile π electrons, the polarisation of single σ bonds being neglected, although the latter may be important for polar molecules, i.e. for the majority of pharmacologically active compounds.

The preferred conformations of GABA and its analogues.

Compound	Method of determination of conformation	Preferred conformation*		References
		coiled	extended	
γ-Aminobutyric acid (GABA)	EHM	—	+ (5.0–6.0)	11
GABA**	CNDO	+	—	10
GABA	LMO	+	—	9
GABA	X-ray diffraction (XRD)	+ (4.5)	—	22, 23
GABA	XRD	—	+	20, 24
Muscimol	EHM	—	+ (5.8)	11
Muscimol	Molecular modelling (MM)	—	+ (5.7)	31
Muscimol	XRD	—	+ (5.77)	32
4-Aminotetrolic acid	MM	—	+ (5.2–6.1)	31, 31, 84
trans-4-aminocrotonic acid	MM	—	+ (5.4–6.3)	84
Hydrazinopropionic acid	EHM	—	+ (5.1–6.1)	38
β-Hydroxy-γ-aminobutyric acid**	EHM	+	+ (5.0–6.0)	51
Homotaurine	EHM	—	+ (5.6–6.6)	38
Homotaurine	XRD	—	+	43
Imidazolylacetic acid	EHM	—	+ (5.5–5.9)	38
Imidazolylpropionic acid	MM	+ (4.3)	+ (5.1–6.3)	53, 55
Imidazolylacrylic acid	MM	—	+ (7.0)	56
α-Guanidinoacetic acid**	MM	+ (3.2–4.8)	+ (5.3–5.7)	54, 56
β-Guanidinopropionic acid**	MM	+ (4.4)	+ (5.7–6.9)	54, 56

*"+" or "–" implies that the given conformation is (or is not) preferred; the distance between N^+ and O^- in Å is indicated in brackets.
**Both conformations are equally probable.

The third quantum-chemical approach to the determination of the GABA conformation employs the method of localised molecular orbitals (LMO), which takes into account configurational and electronic interactions. This method is believed [9,18] to be the most accurate for calculations on highly polarised molecules. The theoretical search for the energetically favourable GABA conformation by the LMO method showed [9] that the folded conformation of the zwitterion is the most stable. The minimum total energy of the extended conformation of an isolated flexible GABA molecule exceeds by 54 kcal mole^{-1} the energy of the folded conformation, which is apparently favoured by the mutual approach of the ionic ends of the molecule in the folded form. The folded conformation is also preferable for the cationic form of GABA (as the hydrogen chloride), although in this case the energy of the extended conformation is higher by only 5 kcal mole^{-1}. Inspection of Dreiding steric models also made it possible to postulate the existence of a folded conformation of the GABA zwitterion with an angle of 40° between the C–N bond and the plane in which the three atoms of the carboxylate group are located, which indicated some interaction between the NH_3^+ and COO^- groups [19].

Conformational analysis of GABA with the aid of X-ray diffraction confirmed that its molecule is fairly flexible and can exist in different conformations [20–24]. In the solid phase GABA forms prismatic crystals with a melting point of 203°C and exists in the zwitterionic form [20–23]. X-Ray diffraction showed that the GABA molecule is to some extent folded with a distance between charge centres of 4.2–5.75 Å [22,23] and that a hydrogen bond with a length of 2.7–3.1 Å can be formed with a deviation from linearity in the N–H...O linkages not greater than by 25°. Nor can one rule out the possibility of the "forking" of the hydrogen bond between adjacent molecules, which is consistent with the melting point [19,22]. The COO^- group is located in the plane passing through the chain of carbon atoms [21,22]. The orientation of this group changes (it becomes almost perpendicular to the given plane) in copper di-γ-aminobutyrate [23]. In the crystalline hydrochloride GABA exists in the cationic form $HOOC(CH_2)_3NH_3^+$. [24] In these crystals the cationic group is always relative to the CH_2COO^- group, while the conformation relative to the $C_{(2)}-C_{(3)}$ bond is either skewed or transoid. Thus both fully extended and partly folded GABA conformations may be found to be preferred in the crystalline state. The zwitterion apparently tends to stabilise the extended conformation, since the oppositely charged atoms of the neighbouring molecules can be located closer to one another than the similar atoms of the same molecule [22].

2. The Conformation of GABA and Its Structural Analogues

Quantum-chemical modelling and X-ray diffraction analysis of GABA make it possible to investigate its static steric structure. However, static stereochemistry does not provide a final answer to the question concerning the conformation of the molecule at the instant when it exhibits its pharmacological activity. Methods for the direct determination of the steric structures of medicinal drugs when the latter act on biological objects have not so far been adequately developed. An indirect approach, which consists in the search for, synthesis, and biological tests of various conformationally constrained analogues of GABA, is therefore extremely fruitful in the solution of stereochemical problems.

Fig. 2 and the Table presents certain fundamental structural GABA analogues exhibiting a GABA-like biological activity. The first of the structural GABA analogues investigated was the natural product muscimol (Fig. 2*b*), which is 5-aminomethyl-3-hydroxyisoxazole, isolated from the fungus *Amanita muscaria* [25]. Johnston et al. [26] suggested that muscimol is an analogue of the fixed extended GABA conformation. Subsequently, in the course of biological tests of this compound, it was found

that, like GABA, it has an inhibiting effect on the central and peripheral neurons [27,28], i.e. it is an agonist of GABA and not its antagonist. The structural analogy between GABA and muscimol is also confirmed by the fact that the latter's bicyclic derivative 4,5,6,7-tetrahydroisoxazolo-[4,5-*c*]pyridine-3-ol proved to be a competitive inhibitor of the absorption of GABA by rat brain sections [29]. In conformity with Dreiding models, the distance between the nitrogen of the tetrahydropyridine ring and the oxygen of the hydroxy-group proved to be 4.4 Å. [30]

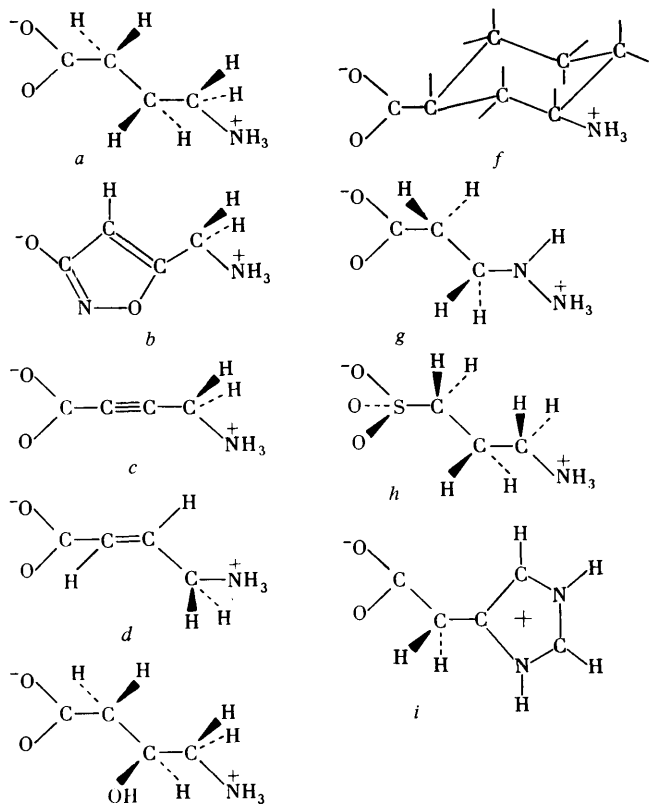


Figure 2. Structural formulae of GABA and some of its agonists: *a*) GABA; *b*) muscimol; *c*) 4-aminotetrolic acid; *d*) 4-amino-*trans*-crotonic acid; *e*) β-hydroxy-GABA; *f*) *cis*-3-aminocyclohexanecarboxylic acid; *g*) hydrazinopropionic acid; *h*) homotaurine; *i*) imidazolylacetic acid.

Theoretical calculations [11] showed that muscimol can assume a conformation analogous to that of GABA, the conformation in which the side chain is coplanar with the five-membered ring and is rotated in the direction of the endocyclic oxygen atom having the minimum total energy. The charged exocyclic oxygen atom is located at a distance of 5.8 Å from the positively charged nitrogen atom. These data suggest, on the one hand, a fully extended chain of carbon atoms in GABA, and, on the other hand, agree with the presence in muscimol of the postulated pharmacophoric GABA group [11]. Steric models showed that the nitrogen atom and the carboxy-group of GABA are isosteric with the exocyclic nitrogen atom and the O–C=N group in the muscimol ring [30]. Such correspondence between the molecular structures of these substances is observed for the extended GABA conformation. X-Ray diffraction studies also indicate the presence of elements of structural analogy between GABA [21] and muscimol [32]. In the crystal state of the latter the side chain is indeed bent in the direction of the oxygen ring atom and makes an angle of 60° with the plane of the ring [32]. The distance between the charged centres in muscimol is then 5.77 Å, which corresponds to the theoretical data [11] for the extended conformation of GABA.

Johnston et al. [30] investigated the relation between the structures of a number of miscimol derivatives and their GABA-like biological activity. An increase in the length of the muscimol side chain by one CH_2 group or substitution of an aliphatic hydrogen atom by the CH_3 group leads to an appreciable lowering of its depressant effect on nerve structures. The substitution of aromatic hydrogen atoms by alkyl groups in muscimol and some of its derivatives led to a sharp decrease of the depressant activity. The authors therefore suggest that the methylidyne group in the 4-position of muscimol is isosteric with the α-methylene group of GABA. The introduction of alkyl groups in the 4-position in the isoxazole ring leads to an increase of its structural rigidity which probably hinders the interaction of substituted muscimol derivatives with the postsynaptic GABA receptors. The study of the biological activities of many muscimol analogues enabled the authors [30] to suggest that different conformers are involved in the absorption of GABA by nerve structures and in its interaction with postsynaptic receptors.

The problem of the preferred GABA conformation was also studied with the aid of its conformationally constrained analogue 4-aminotetrolic acid (4-ATA). [33] In this compound the linearity of the triple bond fixes the positions of the four carbon atoms in such a way that the charged N^+ and O^- centres of the zwitterionic form are located at a distance of 5.2–5.8 Å from one another. The rigid 4-ATA molecule cannot assume a folded conformation and its structure corresponds to the extended GABA conformer. In the study of the action of 4-ATA on the spinal neurons of the cat [34] it was observed that it exhibits between one-half and one-fifth of the activity of GABA on these receptors. Other facts confirming the physiological activity of this compound were also obtained. The GABA-like activity of 4-ATA suggests that GABA exhibits its biological activity in the extended conformation and that the 4-ATA structure apparently includes a GABA-like pharmacophore [11]. This hypothesis received additional experimental confirmation after Johnston et al. [35] synthesised and tested on the same biological objects *cis*- and *trans*-aminocrotonic acids, which are relatively rigid structural analogues of GABA with folded and extended conformations respectively. The *cis*-isomer did not exhibit biological activity, while the *trans*-isomer, which simulates the extended GABA conformer, acted on the central nervous system of mammals just as effectively as GABA. X-Ray diffraction showed that the structure of *trans*-4-aminocrotonic hydrochloride exhibits a definite similarity to that of GABA hydrochloride [20].

The study of other sterically restricted analogues of GABA (see Table) showed [36] that only compounds which simulate the extended GABA conformation and in which the distance between N^+ and O^- differs insignificantly from the corresponding distance in GABA exhibit physiological

activity. Thus, in the series of aminocyclohexanecarboxylic acids, only *cis*-3-aminocyclohexanecarboxylic acid (but not the *trans*-isomer) exhibited a GABA-like activity [36]. The distance between the charges is identical with that in the extended GABA conformation only in the diequatorial conformer.

In the series of piperidinecarboxylic acids, nipecotinic acid (piperidine-3-carboxylic acid), which functions as a strong non-competitive inhibitor of the absorption of GABA by brain sections, is of interest [30]. It possesses conformational rigidity, which can be used in the study of "active" conformations of GABA. In aqueous solution and in the solid state nipecotinic acid exists in the "chair" conformation with the carboxy-group in the equatorial position [30]. The distance between N^+ and O^- in this form of the acid is 4.24–4.76 Å according to NMR and X-ray diffraction data [30].

The discovery of this new inhibitor of the absorption of GABA extended the range of GABA-like compounds. It was found that a series of betel nut (*Areca catechu* L.) alkaloids (arecoline, arecaidine, etc.) combined with nipecotinic acid enhanced the inhibiting effect of GABA on the bioelectrical activity of nerve cells [37].

Kier et al. [38] carried out theoretical calculations on hydrazineopropionic, imidazolylacetic, and 3-aminopropanesulphonic (homotaurine) acids and taurine (Fig. 2 and Table) in order to determine the preferred conformation and the structural elements of similarity with GABA. It has been shown recently [39-43] that these compounds can simulate the specific biological activity of GABA. The results of the calculations [36] demonstrated that the extended conformation is preferred for all the compounds in the zwitterionic form; with the exception of taurine, the extended conformation includes analogous groups, separated from the oxygen atom by an average distance of 5.8 ± 0.2 Å, which are believed [11] to be responsible for the pharmacological activity of GABA. In taurine, where the *gauche*-conformation is energetically more favourable, this distance is somewhat shorter (on average about 5.0 Å). X-Ray diffraction confirmed the existence of the extended conformation in crystalline homotaurine with an analogous N^+-O^- distance [44]. Experimental data for taurine [45] also agree with theoretical calculations [38].

Measurement of the dipole moments of α-, β-, γ-, and ω-aminoacids (up to C_{11}) showed [46,47] that in solution these acids assume mainly the fully extended conformation. Nevertheless, quantum-chemical calculations predict [9,10] that this is not the only possible conformation and there is an extremely high probability that the pharmacological activity is due to the existence of several conformations [48,49]. Indeed, it has been found that in aqueous solutions at pH 7.0 GABA consists of a mixture of both conformers [36,50]. However, it has been suggested [50] that the physiological activity of GABA is associated with the fully extended conformation of its molecule.

Interesting results were obtained [51] in the calculation of the preferred conformation of β-hydroxy-γ-aminobutyric acid (BHGABA), which is an agonist of GABA. [52] Two energetically equally favourable BHGABA conformations have been determined by the extended Hückel method. The first is characterised by an angle of 180° (along the $C_\alpha - C_\beta$ bond), free rotation of the carboxy-group, and a distance of 5.0–6.0 Å between the 'onium group and the oxygen atoms of the carboxy-group. This transoid conformation is consistent with the extended GABA structure predicted theoretically in an earlier investigated [11] and with experimental crystallographic studies [20,21]. An angle of 300° ($C_\alpha - C_\beta$ bond) with a close proximity between hydroxy- and carboxy-groups (apparently by virtue of hydrogen bonding) and with a fixed position of the carboxy-group (an $O=C=C_\alpha$ angle of 120°) is characteristic of the second conformation of BHGABA (the *gauche*-conformation), which corresponds to the folded form of the molecule in crystalline GABA. [19]

Steward and Clarke [53] attempted to establish the relation between the structures of twelve GABA agonists [26,33,53-56] and their activities. Using classical calculations of the potential energy, they determined the probability of the existence of a conformer with minimum energy. Their results are "qualitatively analogous" to data obtained in an NMR study [17] on γ-aminobutyric acid and a number of its agonists. The internuclear distances in various conformational states of the agonists were calculated with the aid of molecular models. The authors [53] took into account the fact that, according to quantum-chemical calculations [57], the charges on the zwitterions are apparently mainly concentrated on the hydrogen atom of the protonated basic group and on the oxygen atoms of the acid groups. On the basis of their calculations, Steward and Clarke [53] concluded that the greatest activity is shown by agonists [22,32,57,58] in which the distance between the zwitterionic charges is approximately 5.4 ± 0.4 Å (see Table). These data support the view that the biological activity of the GABA molecule is associated with its extended conformer.

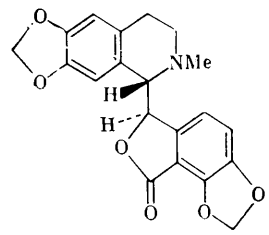


Figure 3. The structural formula of the alkaloid bicuculline.

3. The Conformation of the Alkaloid Bicuculline—a GABA Antagonist

A considerable amount of attention has been devoted recently to the study of the structural characteristics of GABA inhibitors in order to determine the similarity of the agonists and to identify the pharmacophoric group in GABA. The structure of bicuculline—a plant alkaloid of the phthalide–isoquinoline series isolated from *Coridalis species* (Fig. 3), is of greatest interest. Curtis et al. [31] were the first to show that, among the series of alkaloids with convulsant activity which they tested, containing the isoquinoline structure and potentially capable of combining with GABA receptors, bicuculline is the most specific antagonist of the depressant activity of GABA; the antagonism is probably due to the competition for the same receptors on the postsynaptic membrane. The discovery of a selective GABA antagonist stimulated theoretical and experimental studies designed to determine the structural analogy between GABA and its receptor. Attempts were made [19,35] to account for the antagonistic properties of bicuculline in relation to GABA by their stereochemical correspondence, i.e. by the fact that part of the alkaloid

molecule must be isosteric with the biologically active conformation of GABA and certain conformationally constrained GABA analogues [35,60]. This enables the bicuculline molecules to compete with GABA for a proportion of its receptors. Examination of the molecular models of the two compounds showed that the extended (i.e. fully transoid) GABA molecule, containing at its end the nitrogen atom and the carboxylate group O=C−O, can be exactly isosteric with the section of the bicuculline molecule with the nitrogen atom and the O=C−C group [31,35]. The structure of the partly folded GABA conformation is more isosteric with the section of the bicuculline molecule containing the nitrogen atom and the lactone group O=C−O.[19] Subsequent experimental and theoretical studies [61-63] confirmed the correspondence between the steric structures of these sections of the molecules of the two substances and demonstrated the similarity of the charge distribution among the atoms in these groups.

In all probability the early molecular models of bicuculline [19,34] were based on an incorrect configuration of the alkaloid [11] and merely represented its diastereoisomer with a pseudoaxial (and not pseudoequatorial) disposition of the CH_3 group at the nitrogen atom of the piperidine ring [62-64]. However, this should not be reflected in the determination of the isosteric groups of GABA and bicuculline [62]. The absolute configuration of crystalline bicuculline was determined by the analysis of the anomalous dispersion of X-rays [61,65]. Fig. 4*a* illustrates the absolute steric structure of the bicuculline molecule in the crystalline state [61]. The relative configurations of the asymmetric carbon atoms in the molecule are of greatest interest. Fig. 4*b* illustrates schematically the central part of the bicuculline molecule, which is usually compared with the GABA molecule. It has been established that in this conformation of crystalline bicuculline the $N_{(6)}$ and $O_{(3)}$ atoms are antiperiplanar (almost *trans*-) in relation to the $C_{(4)}-C_{(5)}$ bond. The fully extended form of GABA requires only a slight constraint in order to correspond to the bicuculline conformation in the crystalline state. The carboxy-group of GABA is isosteric with the group of $O_{(1)}$, $C_{(2)}$, and $C_{(26)}$ atoms of bicuculline. The conformation of bicuculline corresponding to the extended form of GABA is consistent with data obtained in a study [23] of the steric structure of one of the crystalline forms of the copper(II) complex of GABA.

However, bicuculline hydrochloride and methochloride, which are also biologically active [60], can have other conformations, different from the extended conformation of crystalline bicuculline. Fig. 4*a* shows that the introduction of a proton or a methyl group at the $N_{(6)}$ atom of the alkaloid causes an appreciable steric hindrance between $H_{(19)}$ and $N_{(6)}$, which are separated by a maximum distance of 2.86 Å in the free state. This can lead in its turn to the rotation of the aromatic groups about the $C_{(4)}-C_{(5)}$ bond and to a change in the conformation of the GABA-like fragment of the bicuculline molecule. EHM [51] and LMO [65] calculations as well as ^{1}H NMR data for the protonated form of the alkaloid and its methochloride in aqueous solutions [50,66] were used to determine the preferred conformation of bicuculline. Protonated bicuculline was found to have a preferred conformation with the proton in the *cis*-position relative to the lactone ring [50]. The lowest energy level was observed for the *cis*-position with a dihedral angle between the aromatic rings of approximately 90°. In this conformation the distance between the 'onium group and the carbonyl oxygen is 5.6 Å, which indicates the presence in bicuculline of the structural features and dimensions corresponding to the extended conformation of GABA. Andrews and Johnston's data [66] do not conflict with this hypothesis and show that rotation about the $C_{(4)}-C_{(5)}$ bond is possible (Fig. 4*a*) in the range from −70° to −110°† and that preferred rotational conformers should therefore exist. It was then noted that the free alkaloid in solution can have a conformation different to that of bicuculline salts. Within the limits of the angular rotation indicated, there is a possibility of the attainment of an isosteric correspondence between a fragment of the alkaloid, on the one hand, and the structure of GABA and a number of its agonists (in which there is some variation of the distances between N^+ and O^-), on the other. The N-containing ring of the protonated alkaloid has a preferred "half-chair" conformation with a pseudoaxial disposition of the phthalide ring.

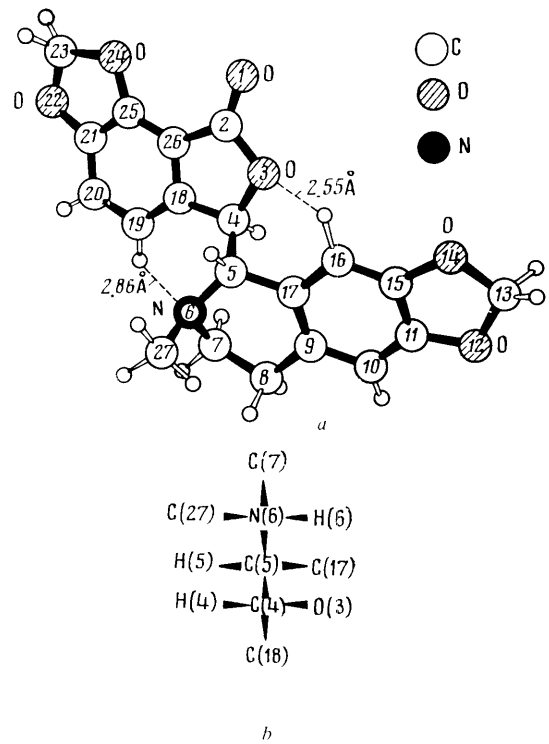


Figure 4. The configuration of bicuculline in the crystal: *a*) absolute configuration; *b*) relative configuration of the asymmetric atoms of the protonated molecule (the numbering of the atoms is in accordance with Gilardi's paper [61]).

The distribution of the charges on the atoms in three-dimensions has a definite importance for the determination of the preferred conformations of bicuculline, for distinguishing GABA agonists and antagonists, and for the elucidation of the mechanism of the interaction of GABA with its receptor. Fig. 5 illustrates the molecular skeletons of GABA (extended conformation) and protonated

† The torsional angle is positive if $N_{(6)}-C_{(5)}$ rotates clockwise about $C_{(4)}-C_{(5)}$.

bicuculline with calculated atomic charges[67]. Calculations have shown[67] that the $O_{(10)}-C_{(11)}=O_{(12)}$ group (Fig. 5*a*) exhibits a greater similarity to the carboxylate group of the GABA zwitterion than does the $C_{(2')}-C_{(11)}=O_{(12)}$ group, the negatively charged atoms of the lactone group of bicuculline (Fig. 5*a*) having smaller charges than the atoms of the GABA carboxylate group (in its partly coiled conformer the charges change insignificantly).

The part of the bicuculline molecule isosteric with GABA contains two asymmetric centres, which corresponds to the possibility of the existence of four optical isomers. Since earlier studies[31,34] were performed on (+)-bicuculline only (Fig. 3), Collins and Hill[68] synthesised by the method of Teitel et al.[69] the methochloride of its (−)-isomer (Fig. 6*a*), which is rarely encountered in nature[70], and tested its biological activity. The results of the tests showed that only the (+)-form of bicuculline methochloride‡ exhibits an antagonistic effect on both the depressant properties of GABA and on its presynaptic inhibition. Furthermore, the (+)-isomer is a stronger convulsant than the (−)-isomer (approximately by a factor of 400). Evidently the conformation of the (+)-isomer is more isosteric with the preferred biologically active conformation of GABA than that of the (−)-isomer.

(+)-Bicuculline has the 1*S*,9*R*-configuration [its (−)-form has the 1*R*,9*S*-configuration[64,73]] and one can probably expect that only analogues with a similar configuration at the asymmetric centres will exhibit a physiological GABA inhibiting activity. The study of the structural and functional analogues of bicuculline will therefore help in the elucidation of the problem of the optical selectivity of this alkaloid and the mechanism of its antagonism. One of such compounds, which has the same configuration as (+)-bicuculline (1*S*, 9*R*),[68] is corlumine[74] (Fig. 6*b*), which, like the methyl ester of bicucine (Fig. 6*c*) is an effective GABA antagonist[60]. However, their close analogues bicucine[75] and laudanosine (Figs. 6*d* and 6*e*) do not exhibit a GABA-inhibiting activity[31,60]. It is therefore of interest to investigate the biological activity of bicuculline epimers and related compounds in order to determine whether the 1*S*,9*R*-configuration can serve as a criterion of antagonism in relation to GABA in this series of alkaloids[60,68].

It has recently been suggested[76] and then confirmed experimentally[77,78] that 2,6-dithia-1,3,5,7-tetraza-adamantane 2,2,6,6-tetraoxide or tetramethylenedisulphotetramine[79] (Fig. 6*f*) can serve as a GABA antagonist. This substance is a powerful convulsant and, like

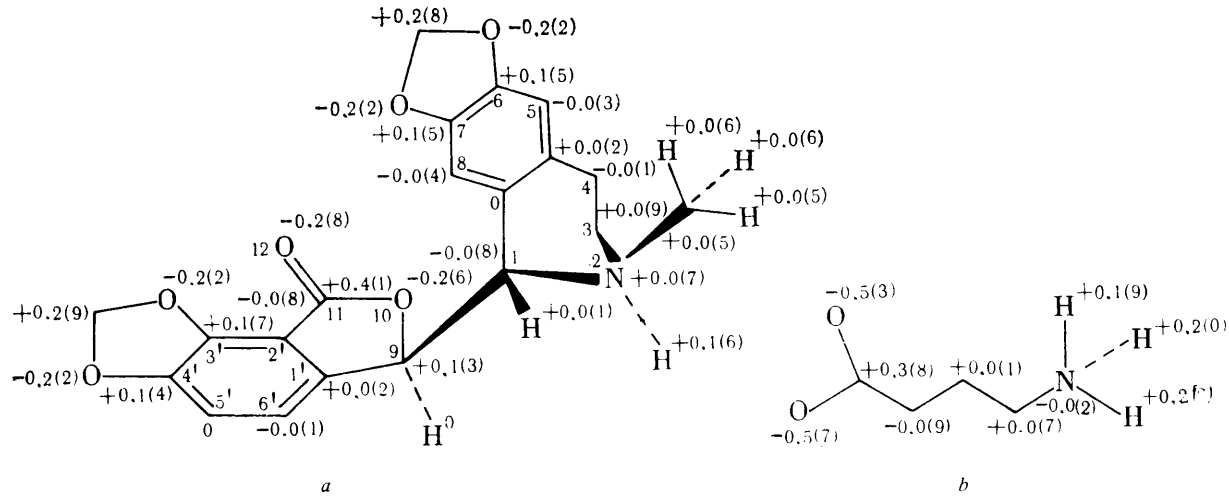


Figure 5. The distribution of charges in bicuculline and GABA: *a*) protonated bicuculline (in the conformation preferred for a solution of the alkaloid); *b*) GABA zwitterion (the numbering of the atoms is in accordance with the paper of Steward et al.[67]).

‡ One should note that the solubility of bicuculline hydrochloride at the "biological" pH is very low and this has led to certain contradictions in the determination of the efficiency of the action of the (+)-form of the alkaloid[17,72]; furthermore, it has been found recently[60] that the (+)-form of bicuculline methochloride is an effective GABA antagonist and is 100 times more soluble in water than the hydrochloride of the alkaloid.

bicuculline, inhibits the depolarising effect of GABA in the sympathetic ganglion of the rat. However, in contrast to bicuculline, the action of tetramethylenedisulphotetramine is non-competitive and probably non-specific. It may be that the nature of its antagonism is different to that of bicuculline[80]. It is noteworthy that pentamethylenemonosulphotetramine (Fig. 6*g*) a very close analogue of the new antagonist, does not exhibit a GABA-inhibiting activity[80]. The study of the nature of the antagonism of tetramethylenedisulphotetramine, which at first sight bears no structural analogy to GABA, is of special interest in connection with the possibility of a new approach to the explanation of the physiological activity of GABA and its analogues.

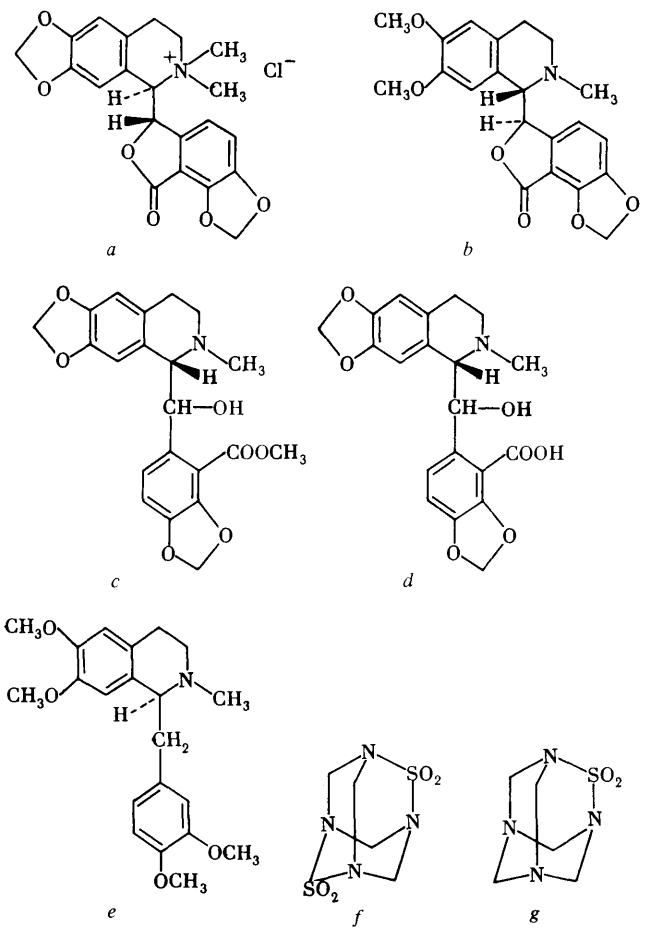


Figure 6. Structural formulae of certain GABA antagonists and their analogues: *a*) (−)-bicucullinemethochloride; *b*) corlumine; *c*) methyl ester of bicucine; *d*) bicucine; *e*) laudanosine; *f*) tetramethylenedisulphotetramine; *g*) pentamethylenemonosulphotetramine.

III. MODELLING OF THE INTERACTION OF γ-AMINOBUTYRIC ACID WITH ITS RECEPTOR

The depressant effect of GABA on nerve structures is achieved by the interaction with its receptor. Information about the chemical nature of GABA receptors is extremely fragmentary and to a large extent speculative. The study of the steric structures of many GABA agonists, which are structurally similar and have a qualitatively similar physiological activity, helps to elucidate in greater detail the structure of the receptors. According to modern ideas, these receptors consist of a protein material[81] in a lipid (hydrophobic) phase, which is located in presynaptic or postsynaptic membranes[82,83]. Receptors capable of capturing GABA can apparently differ from receptors associated with its physiological activity.

One of the probable mechanisms of the interaction of the receptor with the GABA molecule—an agent transmitting the nerve pulse—is based on the idea[49,84] that GABA can exist in the form of two conformers. The receptor initially "recognises" one of the GABA conformations in terms of molecular size, the presence of N^+ and O^- charges, their magnitude, and the distance between them, and attracts this conformation. This is followed by the stage of the interaction of the initial conformer with the receptor, which apparently proceeds with the fixation of a definite GABA conformation on the receptor. The ionised state of the GABA molecule, which varies as a function of the pH of the medium, is responsible for the specific sorption of its molecule on the outer side of the membrane, where sodium is the dominant cation. The sites where GABA is bound to sodium apparently constitute the receptor sections on the membrane where the adsorbed GABA exhibits its physiological effects. This bound form of GABA freely exchanges molecules with the GABA molecules present in solution.

The second conformer can participate in the formation of a GABA – receptor complex in the course of the change of membrane conductivity. The interaction of GABA in a definite "rigid" conformation with the receptor leads to a change in the orientation of the double layer of lipid and phospholipid molecules, an increase of the strength of the bond between GABA and the receptor, and the formation of pores in the membrane. The pore dimensions are determined by the distance between the two charged groups in the GABA molecule, whose position on the membrane is fixed by electrostatic forces and hydrogen bonds. Univalent potassium or chloride ions[85,86], which ensure the inhibition process in neurons, or hydrated sodium ions, responsible for the transmission of excitation[85], enter the cell or emerge from it via the membrane pores. The ability of GABA to exhibit both an inhibiting and an exciting influence on neurons has been observed earlier by Kerkut and Walker[87,88]. The selective change in the permeability of the membrane to various ions is apparently associated not only with conformational changes in the GABA molecule but also with changes in the geometry of the active sections of the receptor, which bears a definite analogy to stereospecific reactions.

The formation of hydrogen bonds ensures the rigidity of the GABA conformer structure within the membrane, which is particularly important in solution, where the GABA molecules can exist in several conformations. The distance between the two charged groups of the extended GABA conformer is between 5.4 and 6.3 Å and, when the conformer reacts with the receptor, it can open pores within the membrane whose size is about 5.4 Å (Fig. 7*a*),[84] which ensures the transport of hydrated sodium ions (whose size is 4.8–5.1 Å) and hence the excitation of the neuron and the transmission of the nerve pulse[89]. In the partly folded GABA conformation the pore size in the membrane diminishes to 4.4 Å (Fig. 7*b*),[84] which is sufficient for the passage of hydrated chloride ions only (their size is 3.32–3.86 Å),[90] the latter being responsible for the

inhibition of nerve signals. This model of the interaction of GABA with the receptor is consistent with all the theoretical and experimental facts obtained previously. Thus the difference between the distances separating the N^+ and O^- charges in a series of GABA agonists showed that the active section in the GABA receptors is somewhat elastic, which permits the variation of the distance between the charged reaction centres of the receptor within a certain range[53]. This idea is consistent with the flexible nature of membrane proteins.

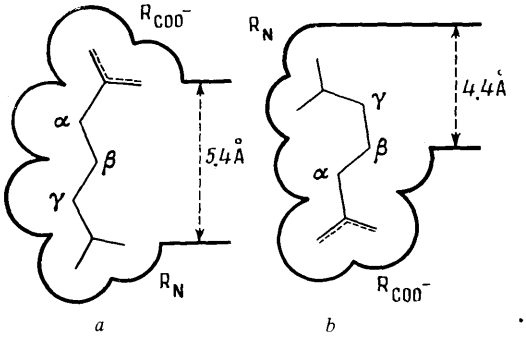


Figure 7. Schematic illustration of the interaction of the conformers of GABA with its receptor (R_{COO^-} and R_N are the active sections of the receptor interacting with a carboxylate and amino-groups of GABA and its analogues)[84]: *a*) extended conformer; *b*) folded conformer.

The inhibiting and exciting effect of GABA on two types of cells in the neurons of the snail *Helix aspersa*[87-89] can be accounted for by the flexibility and the ready change of the structural specificity of this molecule (the interconversion of the conformers) under the influence of external conditions and also by the possibility of structural changes of the receptors themselves in different types of cells[84]. A GABA molecule in the extended conformation interacts with one of the receptors (under these conditions, β-alanine in the two possible conformers of which the N^+-O^- distances are 3.4 and 4.7 Å,[53] does not exhibit a physiological activity, while muscimol is 10–100 times more active than GABA [84]), while the partly folded GABA conformer interacts with the other receptor (in this case β-alanine exhibits a GABA-like activity, while the effectiveness of muscimol does not differ from that of GABA [84]).

The antagonism of bicuculline and related compounds can be associated with the fact that, after the "recognition" by the receptor of the GABA-like element in the alkaloid structure, the latter cannot assume the second conformation[49,53]. This is apparently associated with the charge distribution in the remainder of the cumbersome three-dimensional bicuculline molecule[67]. Its competitive antagonism may depend on the smaller negative charges on the atoms of the lactone ring in bicuculline compared with the COO group in GABA, which leads to a weaker (hindered) binding of the bulky molecule of the alkaloid to the receptor; this weak binding cannot be induced by conformational changes corresponding to the terminal stages in the action of GABA. It has also been suggested[49] that the charges on the residue of the bicuculline molecule can interact with the environment of the active section of the receptor and can thus prevent a rapid liberation of the latter. Furthermore, there is a possibility of a large energy barrier in bicuculline to conversion into another conformer[49]. Bicuculline thus inhibits the activity of GABA, imitating its "initial" conformer and occupying the reaction centres of the receptor without manifesting at the same time a GABA-like physiological activity.

The absence of elements of structural similarity in another GABA antagonist (tetramethylenedisulphotetramine) suggests the possibility of the complete blocking of the receptor and the prevention of access to the latter by GABA molecules as a result of the electrostatic interaction of the charged groups of the receptor and the antagonist. This hypothesis is supported by the non-specificity of the action of the antagonist and the non-competitive antagonism.

Van Gelder[90] suggested a different mechanism for the interaction of GABA with the receptor. According to his model, the inhibition process is associated solely with the configuration at the γ-carbon atom in GABA, namely with the steric influence of the γ-hydrogen atom. When GABA interacts with the receptor, the γ-hydrogen atoms determine the pore dimensions in the membrane, which are 3.7–4.5 Å according to calculations[90], corresponding to the diameter of hydrated chloride ions. However, this theory cannot explain the activity of certain GABA antagonists and also the exciting activity of GABA.[88,89]

In conclusion, the following structural features of compounds with GABA-like activity should be noted.

(1) Free amino- and carboxy-(or sulphoxy-)groups are necessary for the manifestation of GABA activity, because derivatives with ester or amide groups have almost no activity[7]. The comparative ineffectiveness of branched or substituted GABA derivatives can apparently be accounted for by the fact that the substituents interfere with the orientation of GABA relative to the receptor groups.

(2) The optimum length of the atomic chain between the nitrogen of the basic group and the oxygen of the acid group corresponds to four atoms. Molecules with 2–3 or 5–6 atoms in this chain exhibit a low activity or are completely inactive.

(3) GABA receptors react with a molecule having at least two highly charged regions whose charges are of opposite sign to those of the centres of positive and negative charges on the amino- and carboxylate groups respectively.

(4) A GABA-like compound must exhibit a structural stereospecificity, i.e. must correspond to one of the GABA conformations. For activity to be shown, the charges on the cationic (N^+) and anionic (O^-) groups of the zwitterionic form must be at a distance of 5.0–6.0 Å (exciting activity) or 3.7–4.5 Å (inhibiting activity)[84,90].

(5) Not only the properties indicated above are important for the interaction with the receptor; in certain cases the "recognition" of the molecule by the receptor requires a specific optical configuration. In order to account for the chiral specificity of the receptor, further investigation of the physiological activity of alkaloids of the phthalide–isoquinoline series is required.

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The interaction of a biologically active molecule with a macromolecular receptor is possible by virtue of the influence of intermolecular forces and presupposes a definite intermolecular orientation, which apparently does

not rule out a change in the conformation of the molecule when it approaches the receptor, The final solution of the problem of the preferred conformation of medicinal drugs depends on direct experimental observations on the complexes of the active molecules with the receptor. The most promising methods for the determination of the "topography" of the active centres of the receptors and for the elucidation of the mechanism of the action of GABA and other medicinal preparations may be X-ray diffraction and nuclear magnetic resonance of GABA–receptor complexes in the biophase itself. Computer quantum-chemical analysis is of great assistance to chemists, biochemists, and pharmacologists in the solution of these problems. In addition, when account is taken of the influence of the surrounding medium and the receptor on the energetically favourable GABA conformation and of the conformational and electronic changes in the structure of the macromolecular drug–receptor complex for various GABA-like medicinal preparations, such analysis may be used in future to predict and design new effective drugs with a desirable range of action on the central nervous system of man.

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Advances in the Search for Medicinal Drugs Based on γ-Aminobutyric Acid

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Problems associated with the search for new psychotropic agents based on γ-aminobutyric acid—a mediator of central inhibition—are examined, the principles of the rational synthesis of new medicinal drugs in the series of γ-aminobutyric acid derivatives are discussed, and methods for their chemical synthesis are described. Data are presented on the conformation of γ-aminobutyric acid and the structure of its receptor; certain features of the relation between structure and biological activity in the above series of compounds are considered.
The bibliography includes 178 references.

CONTENTS

I. Introduction 679
II. The conformation of GABA and the structure of the GABA-receptor 679
III. γ-Aminoacids with substituents in the hydrocarbon chain 680
IV. Structural analogues of GABA 684
V. Bound forms of GABA 685

I. INTRODUCTION

Since it was observed in 1950 that γ-aminobutyric acid (GABA) is present at high concentrations in the central nervous system (CNS), workers in various fields carried out extensive studies designed to establish the role of this compound in the functioning of the brain. New data have been obtained in recent years showing that GABA is a mediator of inhibition in vertebrates, including mammals [1-3]. The development of improved methods for the identification of GABA and its metabolites yielded additional information about the metabolism of GABA in the central and peripheral nervous systems, about the enzymes involved in its synthesis and decomposition [4], and about the mechanism of inhibition with participation of the GABA system [5]. It was noted that in certain mental illnesses the GABA metabolism is affected [6]. These findings have served in recent years as a basis for a number of hypotheses concerning the pathogenesis of mental illness [7,8], although the use of GABA and its derivatives as medicinal drugs began much earlier. Pharmacological and clinical tests on GABA, begun at the beginning of the 1950s, have been completed by the synthesis of an effective medicinal drug [9], although its application in the treatment of diseases of the nervous system is complicated by the low permeability of the haemato-encephalic barrier (HEB) to this compound. Studies have therefore been carried out for a number of years on the synthesis of substances close to GABA in structure and having an analogous activity as well as GABA derivatives capable of penetrating into the brain and acting on CNS, and a combined investigation of the properties of such substances has been carried out.

The importance of GABA is not apparently restricted to its mediating function. It is encountered not only in the brain but also in other organs, playing a definite role in the metabolism of carbohydrates, aminoacids, biogenic amines, hormones, and phospholipids [10] and serving as a precursor of many physiologically active substances [11]. Studies in recent years demonstrated the important role of GABA in the synthesis of proteins [12,13]. These data lead to the possibility of using GABA derivatives not only as neurotropic preparations but also in many other fields of medicine.

In view of the considerable interest in the study of the mediating function of GABA, the literature on this field is exceptionally extensive. In recent years alone a series of reviews have been published on the physiological role of GABA [1,2], its biochemical functions [4,14], and clinical applications [9,15]. However, the reviews virtually do not reflect problems associated with the chemical aspects of the search for new medicinal drugs based on GABA, although during the past 10–15 years chemists have synthesised a considerable number of derivatives of this aminoacid. In the course of this research extensive data have accumulated on the methods of synthesis, physiochemical properties, and biological activity of the compounds; a survey of these data can play a definite role in the specific search for medicinal drugs based on GABA. The present review is mainly devoted to methods of synthesis and properties of GABA derivatives used as medicinal drugs or studied experimentally on animals, and to the determination of the relation between structure and biological activity in this series; attention has been concentrated on studies carried out in the last 5–10 years.

II. THE CONFORMATION OF GABA AND THE STRUCTURE OF THE GABA-RECEPTOR

It is generally accepted that the physiological action of GABA is similar to that of the "inhibition factor" discovered by Florey in 1953. [16] Until recently it was believed that this factor is identical with GABA. However, in 1975 Florey showed experimentally that the inhibiting action of the inhibition factor is only 35% due to the presence of GABA in it [17]. Aspartic acid, glutamic acid, and taurine, forming part of the factor, exhibit a similar effect (30%); the remainder of the inhibiting effect is apparently due to the presence of β-guanidinopropionic, γ-guanidinobutyric, and γ-amino-β-hydroxybutyric acids [17,18]. A large group of natural and synthetic compounds, similar to GABA in structure and in inhibiting activity, is also known. These findings indicate the possibility of the interaction of GABA and its analogues with the same biochemical system present in the CNS; this system can be defined as the GABA-receptor. A number of studies in recent years have been

devoted to the determination of the characteristics of the structure of this receptor, the methods for its isolation, and the conditions for the interaction of GABA derivatives with it.

On the basis of ideas concerning the complementarity of the structures of the medicinal drug and the receptor, one of the ways of solving the problem of the structure of the GABA-receptor consisted in the investigation of the structural features of GABA and its agonists which ensure the optimum interaction with the receptor. Kier[19] suggested that the energetically preferred conformation of the substance is identical to that in which it interacts with the receptor. This hypothesis was found to be justified in the study of a large and varied group of preparations, including anti-inflammatory, adrenergic histamine derivatives, etc. The preferred GABA conformation was determined by the molecular orbital method (LCAO-MO) taking into account the principle of the minimisation of the total energy of the molecule. Calculations showed[20] that in this conformation the ammonium and α-methylene groups of GABA (I) are in the transoid positions, while the COO^- group can rotate freely. The distance between N^+ and O^- is in the range 5.0–6.1 Å. Calculation on the muscimol (II) molecule, which has an inhibiting effect similar to that of GABA[21] and acts on the same receptor[22], showed that in the preferred conformation the side chain is coplanar with the ring and is directed towards the ring oxygen. In this conformation the charged exocyclic oxygen atom is located at a distance of 5.8 Å from the 'onium nitrogen atom[20]. A similar calculation for a group of GABA-like substances showed that the distance between N^+ and O^- in γ-amino-β-hydroxybutyric acid (III),[23] β-hydrazinopropionic acid (IV), homotaurine (V), and imidazolylacetic acid (VI)[24] is 5–6 Å. It was also established that substances with a "rigid conformation"—γ-aminotetrolic acid (VII)[25] and *trans*-γ-aminocrotonic acid (VIII),[26] which are similar to GABA in its fully extended form and have an N^+–O^- distance in the range 5.2–5.8 Å—have an inhibiting effect similar to that of GABA. In the alkaloid bicuculline (IX),[27] which is a powerful competitive antagonist of GABA[28], the distance between the 'onium group and the oxygen atom of the carbonyl is 5.6 Å. Thus the distances between the charged groups in GABA and in compounds (II)–(IX) are approximately the same, demonstrating the importance of the extended conformation of GABA for its interaction with the central inhibition receptor, whose active section should have two charged regions of opposite sign located at a distance of 5–6 Å from one another. However, van Gelder proposed a folded conformation for GABA with a distance between nitrogen and oxygen atoms of 3.7–4.5 Å.[29] X-Ray diffraction study of the GABA zwitterion in the crystalline state also led to the conclusion that its molecule is to some extent folded[30,31], while crystalline GABA hydrochloride has an extended structure[32]. On the basis of molecular orbital calculations, Pullman suggested a folded conformation for the isolated GABA molecule, which is a consequence of the strong interaction of its two charged ends[33]. From the pharmacological point of view, the conformation in solution, where the inhibiting effect is manifested under physiological conditions, is of greatest importance. According to Pullman's data, a large number of stable conformations of the GABA molecule exist in solution, which apparently enables it to interact with different receptors[33].

During the last 3–4 years a number of publications concerning the direct investigation of GABA by methods used for the choline receptor have appeared[34–39]. Although these studies do not exhaust all the aspects of the problem associated with the structure of the GABA receptor, the information obtained can greatly facilitate the search for new synthetic GABA agonists and antagonists. On the other hand, systematic investigation of the relation between structure and pharmacological activity in this series of compounds makes it possible to obtain a more complete idea about the structure of the GABA receptor.

Among the numerous studies of natural and synthetic GABA analogues, derivatives with substituents in the hydrocarbon chain, compounds with modified COOH and NH_2 groups or with a trimethylene chain (structural analogues), as well as esters and *N*-acyl derivatives of GABA (bound forms) occupy an important place and these will be considered further.

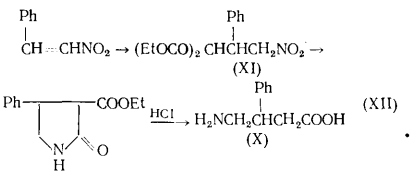
III. γ-AMINOACIDS WITH SUBSTITUENTS IN THE HYDROCARBON CHAIN

The main methods for the synthesis of GABA have been described[9] and they will not therefore be considered in the present review. We need only examine the single-step method for the preparation of GABA[40] by the selective oxidation of *p*-hydroxyphenylpropylamine with ruthenium tetroxide (in 69% yield). Labelled [^{14}C]GABA is synthesised by reducing the ethyl ester of labelled β-cyanopropionic acid under pressure[41]. Selective substitution of α-hydrogen atoms by deuterium yielded α-deutero-GABA in a high yield[42]. Enzymatic decarboxylation of glutamic acid and the microbiological synthesis of GABA from L-glutamic acid or ornithine may be of some interest for the preparation of GABA[43].

Up to the middle of the 1950s, the methods of synthesis of substituted γ-aminobutyric acids were little investigated and only after the mediating function of GABA in mammals had been discovered was the attention of synthetic chemists drawn to this problem. The aim of the investigations was the synthesis of compounds retaining the GABA carbon skeleton and both its functional groups but containing in the side chain lipophilic substituents capable of increasing the solubility of the entire molecule in fats and thus improving its permeation through HEB.

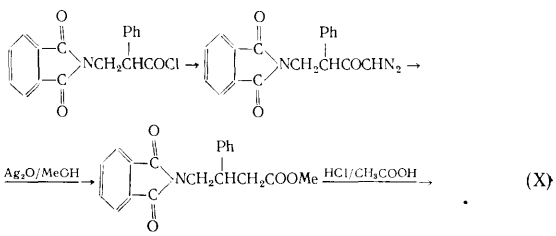
Systematic studies on the synthesis and chemical properties of unsaturated compounds have been carried out for many years in the Department of Organic Chemistry of the Leningrad State Pedagogic Institute, one series of which led to the preparation of GABA derivatives and α-pyrrolidinones. In 1954 Perekalin and Sopovoi[44] synthesised γ-amino-β-phenylbutyric acid (X), the pharmacological study of which demonstrated that it has the properties of a mild tranquiliser[45]. The subsequent cycle of investigations, carried out by members of this Department and the Bekhterev Leningrad Psychoneurological Institute, was completed by the synthesis of a new psychotropic preparation phenybut (β-phenyl derivative of GABA)[46]. A symposium devoted mainly to the chemistry, pharmacology, and clinical applications of Phenybut was held in 1974 in Olaine; the industrial manufacture of this preparation has now been organised. Phenybut was synthesised by the condensation of β-nitrostyrene with diethyl malonate, the subsequent reduction of the resulting ethyl ester of α-ethoxycarbonyl-γ-nitro-β-phenylbutyric acid (XI) in the presence of a nickel catalyst to 3-ethoxycarbonyl-4-phenylpyrrolidinone (XII), and treatment of the latter with 20% hydrochloric acid[44]. In recent years Perekalin and coworkers developed and patented a technological version of this synthetic scheme[47].

Scheme 1



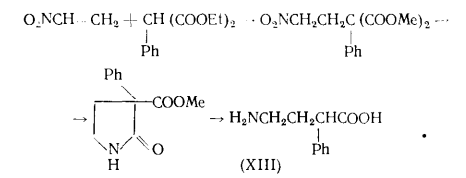
Kupryszewski and coworkers[48] obtained compound (X) by the reduction of β-cyano-β-phenylpropionic acid. A similar method of synthesis of the β-phenyl derivative of GABA by the reaction of phenylacetonitrile with ethyl bromoacetate and subsequent reduction and hydrolysis of the resulting ethyl β-cyano-β-phenylpropionate was described recently[49].

A new synthesis of compound (X) from α-phenyl-β-alanine using the Arndt-Eistert reaction was described in 1974[50]:

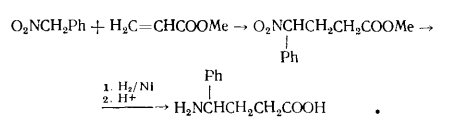


Studies by Perekalin and coworkers, devoted to the development of a general method of synthesis of substituted γ-aminobutyric acids, led to the preparation of various derivatives, which helped to elucidate the relation between the structure and pharmacological activity of compounds of this type. When other nitro-olefins were used instead of nitrostyrene, β-isopropyl, β-*p*-methoxyphenyl, β-*p*-hydroxy-*m*-methoxyphenyl, β-2-furyl and β-2-thienyl derivatives of GABA[51], β-(*o*-tolyl), β-(*n*-tolyl),[52,53] and β-(*p*-tolyl)[54] derivatives, as well as a number of derivatives of γ-amino-β-phenylbutyric acid containing various substituents in the benzene ring[55] were obtained via Scheme 1.

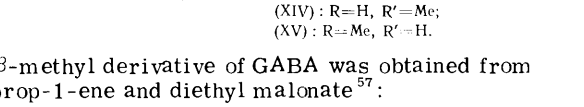
In order to synthesise the α-phenyl derivative of GABA (XIII),[56] nitroethylene was condensed with the phenylmalonic ester and the resulting ester of the γ-nitrocarboxylic acid was reduced to the corresponding ester of α-pyrrolidinone-β-carboxylic acid; hydrolysis of the latter led to compound (XIII):



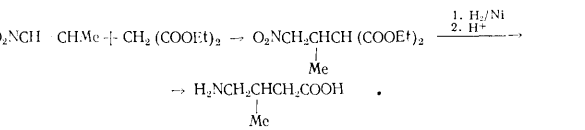
The interaction of phenylnitromethane with methacrylate[52] in the presence of potassium fluoride yielded methyl γ-nitro-γ-phenylbutyrate, which was then converted in the usual way into γ-amino-γ-phenylbutyric acid:



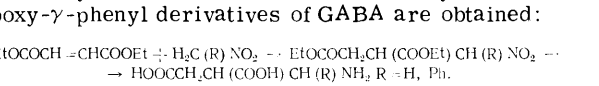
The methyl esters of α-methyl-γ-nitrobutyric acid (XIV) and γ-nitrovaleric acid (XV) were obtained similarly by the nucleophilic addition of nitromethane to methyl methacrylate and of nitroethane to methyl acrylate[57] and were then converted into α- and γ-methyl derivatives of GABA:



The β-methyl derivative of GABA was obtained from 1-nitroprop-1-ene and diethyl malonate[57]:

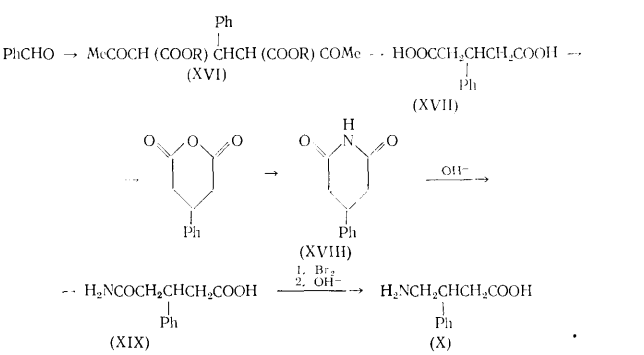


The nucleophilic addition of nitromethane and phenylnitromethane to diethyl fumarate[58] leads to the corresponding nitrodicarboxylic esters from which β-carboxy- and β-carboxy-γ-phenyl derivatives of GABA are obtained:



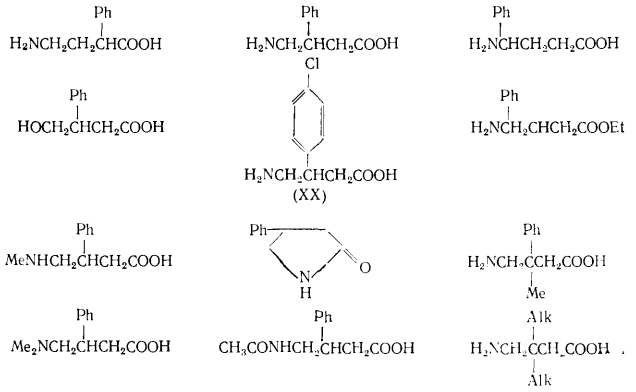
The pharmacological properties of Phenybut have been examined in detail in reviews [1,15] and in another publication[45]. Clinical and pharmacological studies of compounds of this series are still being continued. A report was published in 1975 concerning a comparative study of α-, β-, and γ-phenyl derivatives of GABA and the corresponding lactams. The β-phenyl derivative of GABA proved to be the most active in tests on the potentiation of the effects of barbiturates, ethanol, and morphine[59]. In contrast to the aminoacids, the corresponding lactams exhibited an anticonvulsant activity[60]. Individual compounds of this series were found to possess hypotensive and hypertensive activities[61].

A similar search for medicinal drugs among phenyl derivatives of GABA was carried out in the pharmaceutical chemistry division of the Ciba-Geigy Company[62,63]. γ-Amino-β-phenylbutyric acid (X) was initially synthesised via the mechanism



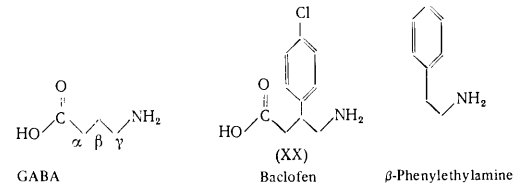
Condensation of 1 mole of benzaldehyde with 2 moles of acetoacetic ester leads to the ester of α,α'-diacetyl-β-phenylglutaric acid (XVI), which splits off both acetyl groups on treatment with alkali and is hydrolysed to β-phenylglutaric acid (XVII). Dehydration and cyclisation of the acid (XVII) in the presence of acetic anhydride and subsequent heating with ammonia lead to β-phenylglutarimide (XVIII), which is then converted into the amide (XIX). After the Hofmann rearrangement, the latter yields γ-amino-β-phenylbutyric acid. Intensive synthetic studies,

carried out by chemists of the Ciba-Geigy Company, led to the preparation of a whole series of GABA derivatives[62,63]:



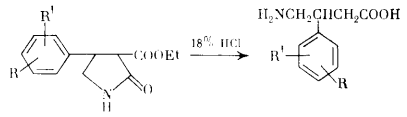
Among the derivatives obtained, capable of permeating through the HEB,[62] γ-amino-β-(*p*-chlorophenyl)butyric acid (XX) showed the greatest pharmacological activity. After extensive clinical tests, it was found that this compound is an effective muscle relaxant, and a preparation based on it began to be manufactured for medical applications under the commercial name Lioresal or Baclofen (the latter name is more common). In 1971 an international symposium devoted to the applications of this preparation in therapeutic practice was held in Vienna. Baclofen is mainly used in the treatment of spastic paralysis[64] including disseminated sclerosis[65]. Reports concerning the use of Baclofen in combination with phenothiazine preparations in the treatment of chronic schizophrenia are of considerable interest[66]. It has been suggested that the use of Baclofen (and a number of other GABA derivatives) in combination with neuroleptic agents ensures a more effective suppression of the dopaminergic mechanisms of the brain and hence a more successful treatment of schizophrenia with a reduced dose of neuroleptic agents[67].

The similarity of the chemical structures of γ-amino-β-(*p*-chlorophenyl)butyric acid and GABA suggested that the mechanism of the action of Baclofen is associated with the activation of the GABA receptor and that it can also influence the GABA formation and degradation processes. However, an experiment on an isolated frog brain established that Baclofen has only a weak inhibiting effect compared with GABA[68]. Furthermore, since the inhibiting effect of Baclofen was not reduced under the influence of bicuculine (a GABA antagonist)[69,70] and strychnine (a glycine antagonist)[69], its action on the CNS cannot be explained by the activation of the GABA and glycine receptors on spinal neurons. The administration of large doses of Baclofen to animals (30 mg kg^{-1}) had no appreciable influence on the GABA concentration in the brain[71]. All these findings give grounds for the hypothesis that GABA and Baclofen act via different mechanisms. It is believed[67] that the action of Baclofen is due to the activation of the adrenoreceptor and not the GABA receptor. Presumably the therapeutic activity of Baclofen as well as Phenybut is associated with the presence of the β-phenylethylamino-group in their molecules, particularly since a similarity has been noted between the inhibiting effects of catecholamines and derivatives of γ-amino-β-phenylbutyric acid[72].



The action of the β-(*m*-chlorophenyl), β-(*o*-chlorophenyl), β-(*p*-fluorophenyl), β-(*p*-isopropylphenyl), and β-(2-naphthyl) derivatives of GABA on the cortical activity in animals has also been studied[72]. All the derivatives investigated exhibited an inhibiting activity which was not weaker than that of Baclofen.

A number of derivatives of γ-amino-β-phenylbutyric acid, including Baclofen, have been suggested as sedatives. They have been synthesised by the acid hydrolysis of 3-alkoxycarbonyl-4-(R,R′-phenyl)-2-pyrrolidinones[73]:



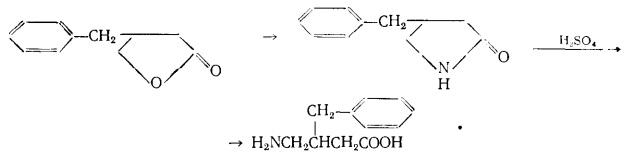
R = H, R′ = *o*-, *m*-, or *p*-Cl; R = R′ = Cl.

An analogous method of synthesising a whole series of β-phenyl derivatives of GABA, consisting in the hydrolysis of the corresponding pyrrolidinones, has been patented[74].

$H_2NCH_2CH(R)CH_2COOH$
R = *o*-ClC_6H_4, *p*-BrC_6H_4, *p*-tolyl, mesityl, *p*-dimethylaminophenyl, *p*-HOC_6H_4, 2-pyridyl, or 3-pyridyl.

In order to elucidate the relation between the structure of a substance and its physiological activity, it may be of interest to investigate the heterocyclic analogues of Phenybut; however, detailed data concerning biological activity are absent from the relevant patent[74] and it is merely stated that all the compounds obtained exhibit a sedative and soporific activity.

A sedative and anticonvulsant activity is also shown by γ-amino-β-benzylbutyric acid, which was obtained by aminating β-benzyl-γ-butyrolactone with liquid ammonia under pressure and subsequent treatment of the resulting 4-benzyl-2-pyrrolidinone with barium hydroxide and sulphuric acid[75]:



4-Phenyl-2-pyrrolidinone, formed on cyclisation of the β-phenyl derivative of GABA[76], as well as 4-(polyalkoxyphenyl)-2-pyrrolidinones also show a psychotropic activity[77].

It is noteworthy that the racemates of the β-phenyl derivatives of GABA were used in pharmacological and clinical tests. In order to investigate the molecular mechanism of the action of these compounds, it is of great interest to study their stereospecificity. The first step in this direction was taken by Kupryszewski and coworkers[78], who were able to resolve the racemic γ-amino-β-phenylbutyric acid into its enantiomers $\{[\alpha]_D = +3.2°$ and $-3.7°\}$ by the fractional crystallisation of the diastereoisomeric salts of γ-amino-*N*-benzyloxycarbonyl-β-phenylbutyric acid with cinchonidine. In order to determine the absolute

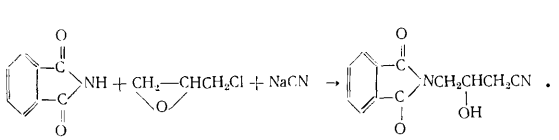
configurations of the enantiomers, they were correlated with β-phenylbutyric acid, the configuration of which is known, by deamination with nitrosyl bromide and subsequent reduction of the resulting γ-bromo-β-phenylbutyric acids with sodium amalgam. It was established that the dextrorotary isomer has the L-configuration (or the *S*-configuration in the Prelog–Kahn system), while the laevorotatory isomer has the D(*R*)-configuration. Khaunina[79] showed that the L-β-phenyl derivative of GABA is twice as active as the DL-compound, while the D-isomer is completely inactive. The increase of activity on passing from the racemate to the L-isomer is not accompanied by an increase of toxicity, which according to the author[79] justifies the assumption that the L-isomer has a greater therapeutic effect and a greater range of the latter compared with the racemate used at the present time. Presumably one of the enantiomers of Baclofen is also more effective than the racemate.

Data concerning the presence of γ-amino-β-hydroxybutyric acid (III) in the brain were first published by Hayashi in 1956, and his subsequent investigations led to the hypothesis that this substance plays an important role in the activity of the brain. It was shown that compound (III) is an extremely interesting pharmacological agent and, under the commercial name Hamibetal, it has now found extensive applications in clinical practice[15]. The β-hydroxy-derivative of GABA was obtained for the first time by Tomita[80] in 1923. In the USSR the synthesis of this preparation, which was given the name Buksamin, was achieved by Mamaev and Shkuro at the Institute of Organic Chemistry of the Siberian Division of the USSR Academy of Sciences[81]. Japanese chemists[82] synthesised compound (III) from GABA, which is chlorinated in the β-position on irradiation with light from a mercury lamp. Treatment of the β-chloro-derivative of GABA with alkali leads to compound (III).

Another method of synthesis, consists in the treatment of γ-chloro-β-hydroxybutyronitrile with hydrogen peroxide and subsequent amination and hydrolysis of the resulting γ-chloro-β-hydroxybutyramide[83]:

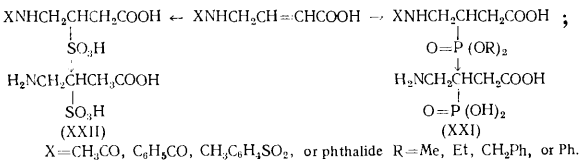
$$ClCH_2\underset{\underset{OH}{|}}{CH}CH_2CN \rightarrow ClCH_2\underset{\underset{OH}{|}}{CH}CH_2CONH_2 \rightarrow \underset{\underset{OH}{|}}{H_2NCH_2CH}CH_2COOH \quad \text{(III)}$$

A convenient method of preparation of compound (III) involves the interaction of epichlorohydrin with phthalimide and sodium cyanide followed by the hydrolysis of the resulting β-hydroxy-γ-phthalimidobutyronitrile[84]:



The β-chloro-derivative of GABA, obtained by treating the methyl ether of the β-hydroxy-derivative of GABA with PCl_5 and the acid hydrolysis of the resulting ester, exhibits an anti-epileptic activity[49].

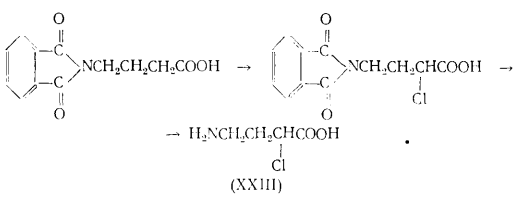
The β-phosphono-derivative of GABA (**XXI**), which exhibits a sedative activity and can be used in the treatment of epilepsy according to the authors, has been synthesised[85] by the reaction of *N*-substituted γ-aminocrotonic acid with trialkyl(allyl)phosphites and subsequent elimination of the protecting groups by refluxing with hydrobromic acid:



X=CH_3CO, C_6H_5CO, $CH_3C_6H_3SO_2$, or phthalide R=Me, Et, CH_2Ph, or Ph.

Treatment of γ-phthalimidocrotonic acid with sodium or potassium bisulphite leads to the β-sulpho-derivative of GABA (**XXII**), which has anti-epileptic and anticonvulsant activities[86].

Among the α-substituted GABA derivatives, the chloro-, amino-, hydroxy-, and mercapto-derivatives (the α-amino- and α-hydroxy-derivatives have been detected in the mammalian brains) have been subjected to extensive pharmacological tests[1]. γ-Amino-α-chlorobutyric acid (**XXIII**) is synthesised by hydrolysing with hydrochloric acid ethyl α-bromo-γ-phthalimidobutyrate, which leads to the replacement of the bromine atom by chlorine together with the removal of the phthaloyl group[87]. An improved method, consisting in the interaction of γ-phthalimidobutyric acid with gaseous chlorine and subsequent hydrolysis with hydrochloric acid, was described in 1971[88]:



(XXIII)

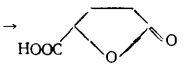
A pharmacological experiment showed that the α-chloro-derivative of GABA apparently permeates readily through the HEB and has a normalising activity in disturbances of the function of the brain[89]. In order to obtain optically active isomers, the phthaloyl derivative of the racemate (**XXIII**) was resolved using quinine[90], but the pharmacological properties of the resulting enantiomers $\{[\alpha]_D^{25} \pm 9.2°\}$ were not described.

α,γ-Diaminobutyric acid is highly neurotoxic[91]. The administration of this compound to animals leads to clonic spasms, which terminate in the death of the animals[92]. This acid is one of the principal structural elements of many peptide antibiotics and this is why its synthesis has been studied in detail[93]. An anticonvulsant activity, comparable to that of the β-hydroxy-derivative of GABA, is shown by the α-hydroxy-derivative of GABA (**XXIV**) when the latter is administered intraabdominally, and its toxicity is smaller than that of GABA; the α-mercapto-derivative of GABA does not exhibit an anticonvulsant activity[94].

A considerable interest has been shown in recent years in the α-hydroxy-derivative of GABA after it was established that new aminoglycosidic antibiotics, butyrosines A and B, which show a high antimicrobial activity, contain this aminoacid. In this connection a whole series of modified aminoglycosidic antibiotics, acylated by γ-amino-α-hydroxybutyric acid, have been synthesised[96–98] and new methods have been developed for the preparation of the aminoacid itself. A simple method for the synthesis of (**XXIV**) involves the replacement of the α-amino-group in α,γ-diaminobutyric acid by the hydroxy-group with the aid of diazotisation[99,100]. Japanese investigators obtained high yields of *R*- and *S*-enantiomers (**XXIV**) by the reaction

of *RS*-α-hydroxy-γ-butyrolactone with potassium phthalimide in dimethylformamide (DMF), the subsequent resolution of the phthalimide derivative into optical isomers via the L-amphetamine salts, and their hydrolysis with hydrochloric acid [101]. When sodium L-glutamate is treated with sodium nitrite and hydrochloric acid, γ-carboxy-γ-butyrolactone is formed and its interaction with ammonia results in its conversion into L-2-hydroxyglutaramic acid; the reaction of the latter with hypochlorite leads to the L-isomer of (**XXIV**) [102]:

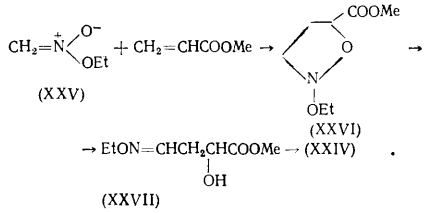
$$NaOOCCH_2CH_2CH(NH_2)COOH \rightarrow NaOOCCH_2CH_2CH(OH)COOH \rightarrow$$



$$\rightarrow HOOCCH(OH)CH_2CH_2CONH_2 \rightarrow H_2NCH_2CH_2CH(OH)COOH.$$

(XXIV)

The L-enantiomer of (**XXIV**) can also be obtained in 15.3% yield by the aerobic fermentation of certain *Acetobacter* strains in a nutrient medium containing the racemic mixture [103]. A fundamentally new method of synthesis of the α-hydroxy-derivative of GABA has been recently proposed by Japanese investigators [104]. The regiospecific dipolar cycloaddition of the nitronic ester (**XXV**) to methyl acrylate leads to the formation of 2-ethoxy-5-methoxycarbonylisoxazolidine (**XXVI**). Heating of compound (**XXVI**) at 100°C leads to the ethoxyimino-compound (**XXVII**), the hydrogenation of which and subsequent acid hydrolysis give rise to γ-amino-α-hydroxybutyric acid [104]:



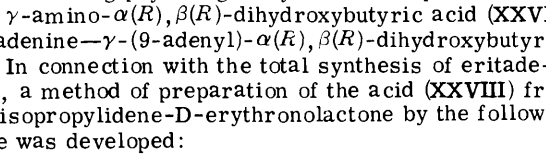
(XXV) (XXVI)

$$\rightarrow EtON{=}CHCH_2CHCOOMe \rightarrow (XXIV).$$

(XXVII)

Using methyl crotonate, α-amino-α-hydroxy-β-methylbutyric acid can be obtained by a similar scheme [104]. One may also note that the reaction of pantolactone (α-hydroxy-β,β-dimethyl-γ-butyrolactone) with potassium phthalimide and subsequent elimination of the phthaloyl group led to the synthesis of γ-amino-α-hydroxy-β,β-dimethylbutyric acid (γ-pantonine)—an analogue of pantoic acid, which is a precursor of panthothenic acid (vitamin B_3). [105]

An interesting physiologically active compound containing γ-amino-$\alpha(R),\beta(R)$-dihydroxybutyric acid (**XXVIII**) is eritadenine—γ-(9-adenyl)-$\alpha(R),\beta(R)$-dihydroxybutyric acid. In connection with the total synthesis of eritadenine [106], a method of preparation of the acid (**XXVIII**) from 2,3-*O*-isopropylidene-D-erythronolactone by the following scheme was developed:



(XXVIII)

Together with a study of β-phenyl derivatives of GABA, the synthesis and pharmacology of the α-phenyl derivatives have been widely investigated [107]. However, the compounds obtained exhibited only a slight stimulating activity, so that further studies on these lines were not continued.

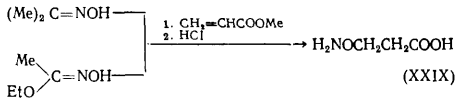
In analysing the available information about the pharmacological properties of GABA derivatives substituted in the carbon chain, one may reach certain conclusions concerning the relation between chemical structure and physiological activity in this series of compounds. The introduction of substituents (chlorophenyl, hydroxy-, sulpho-, and phosphono-groups) in the β-position leads to substances with a strong inhibiting activity. This suggests that such compounds permeate through the HEB, although direct evidence for their penetration into the brain has not been obtained in most cases. The migration of these groups to the α- or γ-position does not affect their permeation through the HEB, but leads to an appreciable decrease of the inhibiting effect, although in many instances the introduction of the substituents in the α-position (chloro-, hydroxy-, and amino-groups) imparts valuable pharmacological properties to the compounds. The presence of the phenyl and alkyl groups simultaneously in the β-position of the GABA molecule as well as one or two alkyl groups does not result in the appearance of neurotropic properties in these compounds. At the same time, γ-amino-α-hydroxy-β-phenylbutyric acid does not differ from γ-amino-β-phenylbutyric acid as regards the intensity of its action on the CNS [108]. An increase of activity was noted after the introduction of substituents into the benzone ring of γ-amino-β-phenylbutyric acid and an appreciable increase was noted for the *para*-derivatives [63].

As already mentioned, the inhibiting effect of HEBA is due to its interaction with the receptor. Presumably β-substitution is most favourable for the retention of the conformation of the molecule which corresponds to the postulated structure of the GABA receptor (this has been demonstrated by calculations for the β-hydroxy-derivative of GABA), and the presence of certain substituents can ensure an additional interaction with the active surface of the receptor. The important role of the steric structure of the molecule is convincingly demonstrated by the finding that pharmacological activity is shown only by one of the stereoisomers of γ-amino-β-phenylbutyric acid.

IV. STRUCTURAL ANALOGUES OF GABA

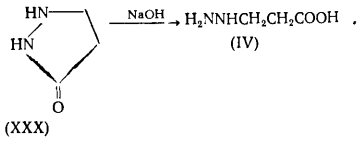
One of the procedures used to synthesise new medicinal drugs with specific activities consisted in the replacement of the CH_2, COOH, and NH_2 groups in the GABA molecule by structurally related groups. Such modifications led in many instances to the formation of substances which inhibit specifically the activity of enzymes involved in the metabolism of GABA and therefore influence its content in the brain. The most interesting substances of this type are isosteric analogues of GABA—β-aminohydroxypropionic acid (**XXIX**) and β-hydrazinopropionic acid (IV), in which the CH_2 group of GABA has been replaced by an oxygen atom and an NH group respectively. These compounds exhibit an exceptionally high inhibiting activity in relation to the GABA transaminase; this activity is determined by the presence of hydroxylamine [109] and hydrazine [110] residues, capable of reacting with the aldehyde group of pyridoxal 5′-phosphate, and also by the similarity of the structures of the compound and the substrate. Presumably compounds (**XXIX**) and (IV), which inhibit the transamination of GABA and thereby increase its content, possess psychotropic activity.

β-Aminohydroxypropionic acid has been synthesised by the Michael reaction of acetoxime [109] or hydroxyiminoacetic ester [111] with methyl acrylate and subsequent elimination of the protecting groups:



(XXIX)

Van Gelder [110] obtained β-hydrazinopropionic acid by hydrolysing 3-pyrazolidinone (**XXX**):



(IV)

(XXX)

Another method of synthesising compound (**IV**) is based on the interaction of β-chloropropionic acid [112] or its t-butyl ester [113] with hydrazine. In the usual methods of administration β-hydrazinopropionic acid permeates through HEB and gives rise to a distinct sedative effect in mice, which is associated, according to the author [114], with the increased content of GABA in the brain.

The synthesis of γ-aminotetrolic acid by the amination of γ-chlorotetrolic acid has been reported [115]:

$$ClCH_2C \equiv CCOOH \rightarrow H_2NCH_2C \equiv CCOOH \rightarrow cis\text{-}H_2NCH_2CH{=}CHCOOH \quad .$$
(XXXI)

The acid (**VII**) is the simplest analogue of GABA with a fixed conformation owing to the presence of an acetylenic bond.

cis-4-Aminocrotonic acid (**XXXI**) has been synthesised by the reduction of compound (**VII**) over 10% palladium on barium sulphate; the *trans*-isomer (**VIII**) is formed on dehydration of γ-amino-β-hydroxybutyric acid with concentrated sulphuric acid. In view of the presence of the double bond, which restricts the mobility of the molecule, compounds (**VIII**) and (**XXXI**) can be regarded as rigid analogues of GABA in the open and folded conformations [26] respectively. In experiments on the upper neck ganglion in rats, analogues of compounds (**VII**) and (**VIII**) exhibit an inhibiting effect similar to that of GABA [116]. The acetylenic derivative (**VII**) is also a powerful competitive inhibitor of GABA transaminase [117]; it is extremely likely that the ethylenic analogue (**VIII**) also suppresses the activity of this enzyme.

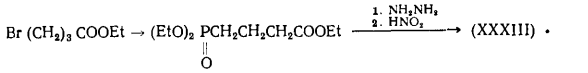
3-Aminopropanesulphonic acid (homotaurine) (**XXXII**), the sulpho-analogue of GABA, has an inhibiting effect [118] and manifests hypotensive and cardiotonic activities [119]. It is stated in a patent [120] that homotaurine is used as a CNS depressant. The anti-epileptic activity of homotaurine has also been reported. The sulphonic acid (**XXXII**) is synthesised by converting 3-aminopropanol into 3-amino-1-chloropropane, which is then treated with sodium sulphite [120]:

$$H_2N(CH_2)_3OH \xrightarrow[\text{or } PCl_5]{SOCl_2} H_2N(CH_2)_3Cl \xrightarrow{Na_2SO_3} H_2N(CH_2)_3SO_3H \quad .$$
(XXXII)

γ-Aminopropylphosphonic acid (**XXXIII**), the phosphono-analogue of GABA, has been obtained by the addition of nitromethane to diethyl vinylphosphonate with subsequent reduction of the nitro-group and the hydrolysis of the phosphonate ester [122]:

$$CH_2{=}CHP(O)(OEt)_2 \rightarrow O_2NCH_2CH_2CH_2P(O)(OEt)_2 \rightarrow$$
$$\rightarrow H_2NCH_2CH_2CH_2P(O)(OEt)_2 \rightarrow H_2NCH_2CH_2CH_2P(O)(OH)_2 \quad .$$
(XXXIII)

The synthesis of compound (**XXXIII**) by the interaction of the γ-bromobutyric acid ester with triethyl phosphite and subsequent Curtius amination has also been described [123]:



(XXXIII) .

Unfortunately the available information about the pharmacological properties of compounds (**VII**), (**VIII**), (**XXIX**), (**XXXI**), and (**XXXIII**) is extremely limited or is altogether lacking.

The replacement of the NH_2 group in GABA by OH leads to γ-hydrobutyric acid. In the form of its sodium salt, this compound is widely used in medicine as a relatively non-toxic non-inhalation narcotic. A number of reviews have been devoted to studies on this preparation [124,125].

V. BOUND FORMS OF GABA

In the course of its metabolism in the brain tissue GABA is deaminated, which leads to the formation of γ-hydroxybutyric acid and the semialdehyde of succinic acid [1]. In the animal and human organisms there are other ways of utilising this compound which lead to physiologically active bound forms of GABA. The content of these substances in the brain varies from 0.0002 to 0.012%, but the specific metabolic pathways leading to the formation of the majority of them have not been investigated; very little is known about their physiological importance in the normal functioning of the brain. An experimental study of the bound forms of GABA showed that they possess valuable pharmacological properties and the possibility of their use in medical practice continues to be investigated. An extremely promising pathway in the search for new medicinal drugs based on GABA was found to involve the chemical combination of the GABA molecule with other physiologically active substances via the amino- or carboxy-groups, which tends to decrease the polarity and in many cases to enhance the lipophilic properties of the molecule and leads to substances which readily permeate through HEB and exhibit a predominantly central activity.

The esterification of GABA yielded its esters, which, when administered in the usual way, exhibited a distinct neurotropic activity similar to that of GABA itself [126]; the highest activity in doses much below the toxic level is shown by the cetyl ester, which has the longest chain among all the esters investigated [127], with the exception of the octadecyl ester [128]. γ-Aminobutyrylcholine, the choline ester of GABA, which has been detected in mammalian brains, has an inhibiting effect in various parts of the brain [129]. Howells [130] believes that γ-aminobutyrylcholine is a mediator of the inhibition in the nervous system, since it exhibits a greater degree of stereochemical similarity to bicuculline, a specific GABA antagonist, than γ-aminobutyric acid; however, this hypothesis did not receive additional experimental confirmation. Very few data are available on the pharmacological effect of γ-aminobutyrylcholine, which is apparently associated with its high toxicity (600 times greater than that of GABA [131]); it has an anticonvulsant activity [129].

γ-Guanidinobutyric acid (**XXXIV**), the guanidine derivative of GABA, has been detected in various animal organs, including the brain. It has been suggested that this compound is formed in the animal organism when GABA combines with the guanidino-group of arginine and that it is subsequently cleaved with formation of urea and GABA. In contrast to GABA, compound (**XXXIV**) has a stimulating

effect on the CNS.[132] γ-Guanidino-β-phenylbutyric acid exhibits a central activity, although it is weaker than that of γ-amino-β-phenylbutyric acid[63]. It has been shown recently that the amide (**XXXV**) lowers the content of urea and glucose in the blood of diabetics[133]. The acid (**XXXIV**) has been synthesised by the interaction of GABA with *O*-methylisothiourea[134]; the amide (**XXXV**) has been obtained in the usual way via the ester (**XXXVI**)[135]:

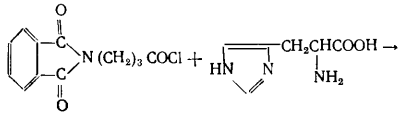
$$H_2N(CH_2)_3COOH \rightarrow \underset{\underset{NH}{\|}}{H_2NCNH}(CH_2)_3COOH \rightarrow$$

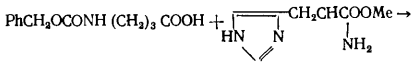
(XXXIV)

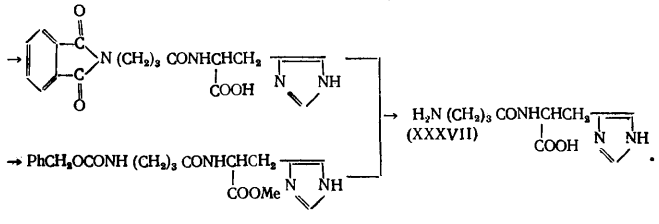
$$\rightarrow \underset{\underset{NH}{\|}}{H_2NCNH}(CH_2)_3COOMe \rightarrow \underset{\underset{NH}{\|}}{H_2NCNH}(CH_2)_3CONH_2 \quad .$$

(XXXVI) (XXXV)

During the last 15 years, a series of γ-aminobutyric acid dipeptides, including γ-aminobutyryl-L-histidine, homocarnosine (**XXXVII**), γ-aminobutyryl-*N*-methylhistidine, homoanserine, and α-(γ-aminobutyryl)-L-lysine (**XXXVIII**), have been detected in the brain tissues of various animals. Homocarmosine was isolated for the first time from ox brain in 1961 and was later detected in the brains of other animals (in appreciable amounts in the human brain). The pharmacological properties of homocarmosine, particularly its action on the CNS, have been described[136]; the anticonvulsant activity of homocarnosine had been noted earlier[137]. Together with carnosine and other histidine peptides, this compound has been proposed as one of the agents for increasing the resistance of the human and animal organism to various bacterial infections[138]. It is synthesised by the usual methods for the synthesis of peptides. The reaction of *N*-phthaloyl-γ-aminobutyric acid with L-histidine and the subsequent removal of the phthaloyl protective group lead to the dipeptide (**XXXVII**). In another procedure the *N*-benzyloxycarbonyl derivative of GABA is condensed with the methyl ester of L-histidine in the presence of ethyl chloroformate and homocarnosine (**XXXVII**) is obtained in high yields after the removal of the protective groups[139]:







The *p*-nitrophenyl ester of the *N*-benzyloxycarbonyl derivative of GABA can also be used as the starting compound for the synthesis of compound (**XXXVII**)[140].

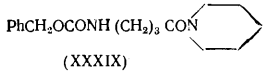
Nakajima's group detected in the rabbit brain tissues[141] and isolated in a crystalline form[142] a dipeptide which was identified as α-(γ-aminobutyryl)lysine (**XXXVIII**). The concentration of this peptide in the brain is much lower than that of homocarnosine; it has been noted that its content in the brain and in the cerebrospinal fluid of the adult man is higher than in children, while the content of homocarnosine in the same tissues is higher in children[142]. It may be that the level of peptides (**XXXVII**) and (**XXXVIII**) in brain tissues is physiologically important, but their function has not so far been established. α-(γ-Aminobutyryl)-L-lysine has been synthesised by the mixed anhydride method involving the condensation of the *N*-benzyloxycarbonyl derivatives of GABA and L-lysine in the presence of ethyl chloroformate followed by the removal of the protective groups over palladium oxide[141]:

$$PhCH_2OCONH(CH_2)_3COOH + \underset{\underset{COOH}{|}}{H_2NCH}(CH_2)_4NHCOOCH_2Ph \xrightarrow[2.\ H_2/PdO_2]{1.\ ClCOOEt} \rightarrow$$

$$\rightarrow H_2N(CH_2)_3CONH\underset{\underset{COOH}{|}}{CH}(CH_2)_4NH_2 \quad .$$

(XXXVIII)

Fosker and Low[143] obtained various glutamyl derivatives of GABA in the hope that these would permeate through the HEB and would serve as an additional source of GABA; however, the compounds obtained were inactive in the biological systems tested. *N*-Benzyloxycarbonyl-γ-aminobutyric acid, which is an intermediate in the synthesis of GABA peptides, has a distinct anticonvulsant activity according to the corazole spasm and electric shock tests[94]; this is probably associated with the improvement of the transport of GABA to the brain. *N*-Benzyloxycarbonyl-γ-aminobutyrylpiperidine (**XXXIX**), which exhibits analgesic and antiacetylcholine activities, is obtained by the reaction of the *N*-benzyloxycarbonyl derivative of GABA with piperidine in the presence of condensing agents[144]:



(XXXIX)

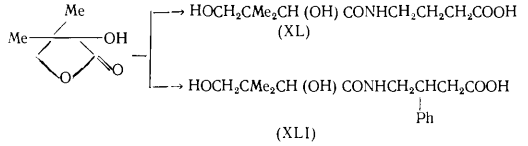
Perekalin and coworkers[145] achieved the synthesis of the dipeptides of γ-amino-β-phenylbutyric acid in order to prolong its action and to improve its permeation through the HEB. The condensation of the methyl ester of γ-amino-β-phenylbutyric acid with the *N*-benzyloxycarbonyl derivatives of α-, β-, and γ-aminoacids or of the methyl esters of α-, β-, and γ-aminoacids with *N*-benzyloxycarbonyl-γ-amino-β-phenylbutyric acid in the presence of phosphoryl chloride leads to the corresponding protected dipeptides, whose acid hydrolysis removes the protective groups and leads to the formation of the free dipeptides.

D-*N*-pantoyl-γ-aminobutyric acid (homopantothenic acid) (**XL**), which is a natural homologue of D-pantothenic acid (vitamin B_3), has been found in animal brain tissues, where it is present in amounts of 4–5 μg per gram of tissue[146].

It has been reported that the acetone powder of calf brain tissue contains an enzyme which can catalyse the condensation of pantoic acid and GABA, resulting in the formation of D-homopantothenic acid[147]; a similar enzyme has also been detected in rats[146]. However, the above synthetase has not been isolated in a pure form and its specificity has not been studied. A doubt has been expressed in a review[4] concerning the presence of homopantothenic acid in the brain.

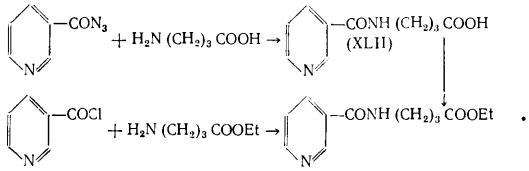
Homopanthothenic acid readily permeates into the brain[148], which indicates the importance of the pantoyl component of the molecule in passing through the HEB-lipid membrane. The distribution of [^{14}C] homopantothenic acid in various components of the mouse brain after parenteral administration[149] and its pharmacodynamics in the mouse brain have been recently investigated[150]. Extensive studies have been carried out on the biological properties[148] and therapeutic action[148,151] of compound (**XL**); the results suggest that the preparation is a new effective

medicinal drug. The acid (XL) is synthesised by condensing D-pantolactone with GABA salts [152-154]. The introduction of the phenyl residue into the β-position of the aminoacid component of D-homopantothenic acid greatly increased its anticonvulsant activity, antagonistic in relation to thiosemicarbazide. The D-pantoyl derivative of γ-amino-β-phenylbutyric acid (XLI) has been synthesised by the action of D-pantolactone on γ-amino-β-phenylbutyric acid in the presence of diethylamine [155]:

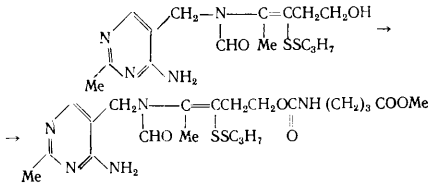


(XLI)

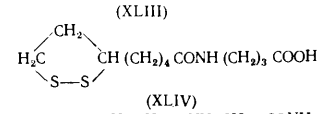
One of the hypotheses concerning the causes responsible for mental illness, put forward by Pauling [156], attributes them to the disturbance of the optimum concentration of vitamins in the brain and it is suggested that high doses of vitamins be used in its treatment. In particular, it has been shown that the use of ultralarge doses of pantothenic acid [157] and particularly nicotinic acid [158] is helpful to schizophrenics. These ideas constitute the basis of the search for new neurotropic substances based on GABA and vitamins, taking into account also the transport functions of certain vitamins and their influence on the nervous system. In particular, it appeared useful to investigate the pharmacological properties of the nicotinoyl derivative of GABA (XLII), which was obtained by the reaction of nicotinoyl azide with GABA; its ethyl ester was synthesised by condensing nicotinoyl chloride with a GABA ester or by esterifying the acid (XLII). [159]



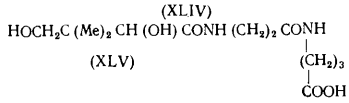
The nicotinoyl derivative of GABA and its ester exhibit a high physiological activity [160]. The GABA derivative of thiamine (XLIII) was synthesised for pharmacological study. When thiamine propyl disulphide is acted upon by phosgene, the product is *O*-chlorocarbonylthiamine propyl disulphide, the reaction of which with the methyl ester of GABA gives rise to the corresponding urethane derivative (XLIII) [161]:



(XLIII)



(XLIV)

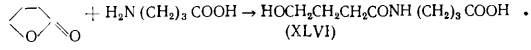


(XLV)

The detoxicating activity of the *N*-α-lipoyl derivative of GABA (XLIV) in poisoning with mercury and arsenic has been reported [162]. Compound (XLIV) has been obtained by condensing the mixed anhydride of α-lipoic acid [163] or its chloride [164] with GABA.

The *N*-D-pantothenoyl derivative of GABA (XLV) has been synthesised by the reaction of the mixed anhydride of D-pantothenic and ethylcarbonic acids with GABA [164]. There is no doubt that extensive investigation of the pharmacological properties of compounds (XLIII)–(XLV) as well as derivatives of GABA combines with other vitamins can be of great practical interest.

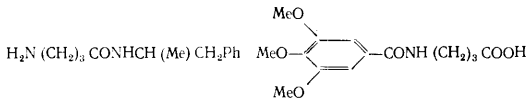
The addition of the GABA molecule to certain biologically active substances also resulted in many instances in the formation of compounds having different spectra of pharmacological activity. Bearing in mind the relatively high permeating capacity of γ-hydroxybutyric acid (GHBA) and its high neurotropic activity, γ-amino-γ-hydroxybutyrylbutyric acid (XLVI) was synthesised by condensing γ-butyrolactone with GABA [165,166]:



(XLVI)

The intra-abdominal administration of (XLVI) has a stronger sedative and hypothermic effect than the administration of GHBA or GABA. This is apparently due primarily to the specific influence of the entire molecule of the γ-hydroxybutyryl derivative of GABA on membranes and energetic processes in the brain tissue and not the activity of its decomposition products [167].

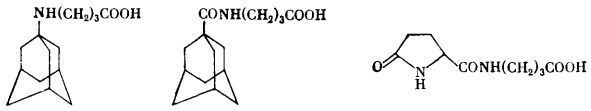
Gamophen (XLVII), the product of the condensation of GABA with phenamine, readily permeates through HEB and inhibits the orienting effects in white mice. The preparation has a hypothermic activity and potentiates the action of barbamyl and chloral hydrate, but, in contrast to the majority of depressants, it enhances the convulsant activity of corazole [168].



(XLVII) (XLVIII)

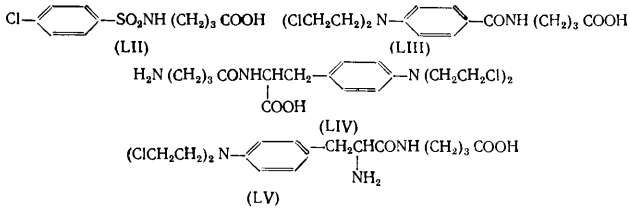
3,4,5-Trimethoxybenzoyl-γ-aminobutyric acid (XLVIII), which is a derivative of gallic acid, effectively prevents and suppresses in a pharmacological experiment (in doses of 100 μg kg^{-1}) the muscular tremor in white mice induced by tremorine or oxotremorine. Preliminary kinetic experiments demonstrated the possibility of using this compound in the treatment of Parkinson's disease [169] and the myocardial infarct [170]. The derivative (XLVIII) has been synthesised by the Schotten–Baumann acylation of GABA with 3,4,5-trimethoxybenzoyl chloride [171] or by the reaction of the mixed anhydride of 3,4,5-trimethoxybenzoic and ethylcarbonic acids with the ethyl ester of GABA followed by the hydrolysis of the resulting ester [170].

The introduction of the adamantyl group into the GABA molecule gives rise to γ-(1-adamantylamino)butyric acid (XLIX), which can be used in the treatment of Parkinson's desease [172]. However, it has been reported [128] that the ethyl ester of this acid does not exhibit signs of neurotropic activity. Together with antibiotic activity, the adamantoyl derivative (L) [173] exhibited a sedative effect [174]. The amide derivative of L-pyroglutamic acid and GABA (LI) shows a psychotropic activity [175].



(XLIX) (L) (LI)

In order to obtain new antidiabetic agents, the *N*-(*p*-chlorobenzenesulphonyl) derivative of GABA (**LII**) was synthesised among other compounds [176]. Attempts have been made to use GABA derivatives as antitumour agents by inserting GABA into the structure of a carcinolytic agent. GABA peptides containing the cytotoxic *N*-bis-(2-chloroethyl)amino-group, namely compounds (**LIII**) [177], (**LIV**), and (**LV**) [178], exhibited a high and selective antitumour activity.



(LII) (LIII)

(LIV)

(LV)

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Thus the study of the pharmacological properties of a large number of GABA derivatives made it possible to discover and introduce into medical practice many effective preparations and to obtain much information about the relation between structure, physicochemical properties, and activity. In particular, it has been shown that the most active substances with depressant activity are those with substituents in the β-position and free amino- and carboxy-groups. Some data show that the manifestation of the pharmacological activity of GABA requires the presence of free amino- and carboxy-groups. At the same time, many natural and synthetic amides or esters of GABA have valuable pharmacological, including neurotropic, properties; on the one hand, this can be due to their high capacity for permeation through biological membranes with subsequent hydrolysis of the ester or amide group in the organism and, on the other hand, it may indicate the importance of the properties of the residue introduced into the GABA molecule. Analysis and survey of the results obtained empirically can play an important role in promoting a more rational synthesis of physiologically active GABA derivatives. However, the most important condition governing the specific search for new psychotropic preparations in this series is the elucidation of the molecular mechanisms of the action of GABA and its active derivatives.

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The Reactivity of Aromatic Dialkenyl Compounds in Polymerisation Reactions

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An attempt has been made for the first time to survey and describe systematically data on the characteristics of the polymerisation of aromatic dialkenyl compounds. The mechanisms of radical, cationic, and anionic polymerisations of these compounds as well as the structures of the resulting polymers, which are of theoretical and definite practical interest, are examined.
The bibliography includes 36 references.

CONTENTS

I. Introduction 692
II. Radical polymerisation 692
III. Cationic polymerisation 693
IV. Anionic polymerisation 694
V. The dilithium catalyst based on *m*-diisopropenylbenzene 697

I. INTRODUCTION

Aromatic dialkenyl monomers (divinylbenzene and diisopropenylbenzene) are of interest for the synthesis of polymers of various structures by virtue of their ready availability and relative resistance to spontaneous polymerisation.

p-Diisopropenylbenzen (*p*-DIPB) polymerises in the presence of cationic catalysts to saturated and unsaturated polymers containing benzene rings in the main chain. In contrast to the *m*- and *p*-isomers, the radical polymerisation of *o*-divinylbenzene (*o*-DVB) yields a partly cyclised polymer. Anionic processes initiated by organolithium compounds give rise to considerable possibilities for the controlled synthesis of polymers with a definite set of properties, block copolymers, reactive oligomers, and polyfunctional polymerisation catalysts.

The relative reactivity of monomers in polymerisation depends on the polarity of the double bond, the stability of the active species formed when the monomer adds to the growing chain, and the steric hindrance in the transition state. In considering the radical, cationic, and anionic polymerisations of aromatic dialkenyl compounds, we therefore took these factors into account.

II. RADICAL POLYMERISATION

The reactivity of substituted styrenes in radical polymerisation has been widely studied[1]. Styrene is known to have a high electron density in the double bond (−0.80). The benzyl radical is greatly stabilised as a result of conjugation with the benzene ring. Depending on the type of group introduced and its position, in ring-substituted styrenes there is a possibility of both an increase and a decrease of the resonance stabilisation of the radical. The replacement of the hydrogen in the vinyl group of styrene can also influence the polarity of the monomer, the resonance stabilisation of the corresponding radical, and the steric hindrance in the transition state. Thus the presence of the methyl group in the α-position makes the vinyl group more electronegative but less reactive than the vinyl group in styrene, which can be due to steric hindrance.

A substituent in the *para*-position is known to influence the reactivity of styrene; *meta*-substitution has little or no influence on its reactivity. Hart[2] explains this difference by the fact that the *meta*-isomer is incapable of involvement in the resonance stabilisation of the charge, while the *para*-isomer is involved in this type of stabilisation.

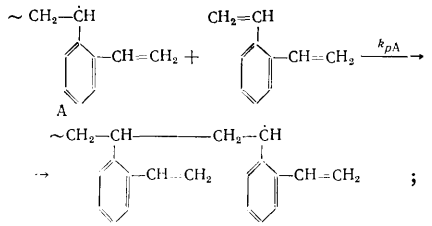
In radical polymerisation the propagation rate constants for the given polymer depends both on the reactivity of the monomer itself and on the reactivity of the radical formed from it. Thus an increase of conjugation energy, which tends to increase the stability of the radical, also increases the reactivity of the initial monomer[3].

It has been shown[4] that *m*- and *p*-divinylbenzenes are fairly actively involved in copolymerisation with styrene, forming three-dimensional copolymers. The copolymerisation of *m*- and *p*-divinylbenzenes with styrene, initiated by benzoyl peroxide, has been studied[5]. Analysis of the copolymer for a degree of conversion of 2−3% led to the following constants for the copolymerisation of styrene (r_1) with *m*-divinylbenzene (r_2) and of styrene (r_1') with *p*-divinylbenzene (r_3): $r_1 = 0.54$; $r_2 = 0.58$; $r_1' = 0.15$; $r_3 = 1.22$, i.e. the vinyl group in *p*-divinylbenzene is more reactive than in *m*-divinylbenzene.

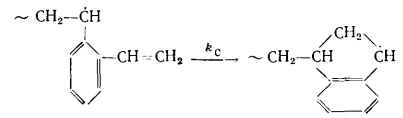
There is a reversal of reactivities in the homopolymerisation of *m*- and *p*-divinylbenzenes using isobutyrodinitrile as the initiator: *m*-divinylbenzene is more reactive than *p*-divinylbenzene, i.e. the alkenyl group in the *para*-position has a stabilising influence on the *p*-divinylbenzene radical[6]. The homopolymerisation of *p*- and *m*-divinylbenzenes has also been studied in the presence of benzoyl peroxide up to the gel point[7]. It was shown that the *meta*-isomer is also more reactive.

In contrast to *m*- and *p*-divinylbenzenes, the polymerisation of *o*-divinylbenzene yields in most cases soluble polymers containing five-membered rings and double

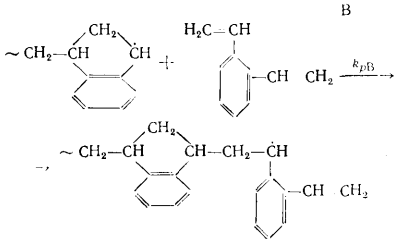
bonds in the side chain. *o*-Divinylbenzene has been polymerised at different temperatures in the presence of α,α'-azobisisobutyronitrile in benzene [8]. The residual unsaturation was determined spectroscopically and by bromination in CCl_4. The study led to three chain propagation mechanisms:



(1)



(2)



(3)

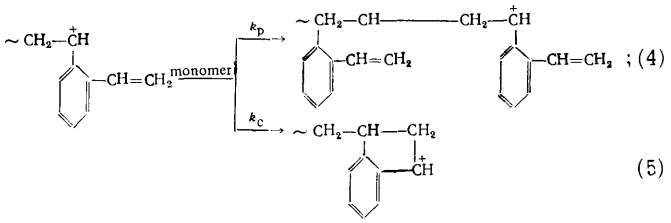
The content of monomeric units with vinyl groups diminishes with increase of the concentration of the monomer in the initial mixture and with increase of polymerisation temperature, since favourable conditions are then created for cyclisation. This finding can be explained by the difference between the activation energies for the propagation of the polymeric chain [reaction (1)] and for the intramolecular cyclisation reaction [reaction (2)]: the growing radical A has a somewhat greater resonance energy than the styrene radical and the cyclic radical B has a smaller resonance energy.

Like other allylic compounds, DIPB has a mobile hydrogen atom at the α-carbon atom. As a result of this, the copolymerisation of various monomers with DIPB leads to copolymers with a low molecular weight [9-11]. The rate constants for chain transfer to DIPB, found from the dependence of the degree of polymerisation of styrene on the concentration of the divinyl monomer in the initial mixture, have been published [12]. They are $8.59 \times 10^{-2} \pm 1.5 \times 10^{-5}$ for *m*-DIPB and $8.43 \times 10^{-2} \pm 3.6 \times 10^{-5}$ for *p*-DIPB (evaluated by the method of least squares), i.e. they are fairly large and almost equal, regardless of the position of the isopropenyl groups in the benzene ring.

III. CATIONIC POLYMERISATION

The cationic polymerisation of aromatic dialkenyl hydrocarbons was studied previously [13,15] in relation to *o*-divinylbenzene and *p*-di-isopropenylbenzene.

It is suggested that the *o*-divinylbenzene chain propagation reaction includes two competing stages: intermolecular propagation [reaction (4)] and intramolecular cyclisation [reaction (5)]:



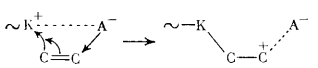
(4)

(5)

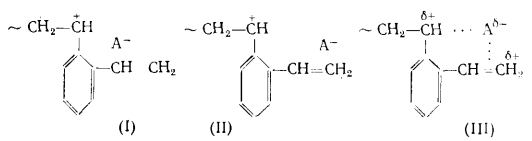
The cyclisation constant is defined as the ratio of two constants:

$$r_c = \frac{k_c}{k_p}$$

In cationic polymerisation, particularly in media with a low dielectric constant where the counterion is linked to the growing centre, the step involving the growth of the polymeric molecule can be represented as a result of the concerted donor–acceptor action by the carbonium ion–counterion pair on the double bond of the monomer:



The structure of the growing ion pair therefore depends on the nature of the anion. Thus the following cases are possible:



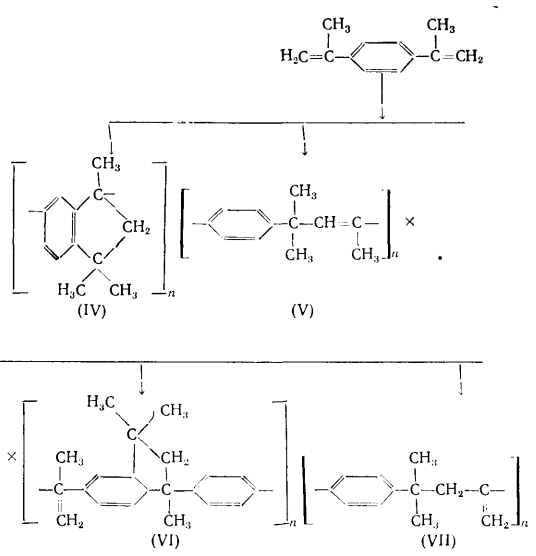
(I) (II) (III)

(Here A^- is the counterion).

An interesting correlation has been found between r_c and the primary ionisation potential of the metal [13,14]. Thus the sequence of primary ionisation potentials Al > Ti > Sn > Fe > B > Zn agrees with the variation of r_c (excluding Ti and Sn). Strong Lewis acids lead to the ion pair (I) and a low value of r_c. [15] The weak interaction of the cation with the counterion permits the formation of the active cation (II) or the spreading of the positive charge to the vinyl group of (III) which failed to react. In polar highly solvating media the carbonium ion can form a free ion pair. The interaction with the vinyl group is therefore evidently replaced by the interaction with the molecules of the polar solvent, reducing the contribution of intramolecular cyclisation. The constant r_c increases with increasing temperature: 0.22 mole litre^{-1} at −20°C and 1.2 mole litre^{-1} at 20°C [15] (for divinylbenzene).

It has been shown [16,17] that *p*-DIPB polymerises under the influence of a cationic catalyst ($TiCl_4$, $SnCl_4$) to saturated and unsaturated polymers containing benzene rings

in the main chain:



(IV) (V)

(VI) (VII)

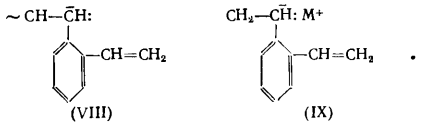
The polymers obtained exhibit a high heat resistance and thermal stability. It has been established on the basis of infrared spectroscopic data [17] that the saturated polymers have structure (IV) (an indan structure), while unsaturated polymers have structures (V)–(VII).

IV. ANIONIC POLYMERISATION

Evidently the possibility of the interaction of the π electrons of the double bond with the active centre in cationic polymerisation promotes cyclisation, whereas this type of interaction is less likely in anionic polymerisation. The polymerisation of *o*-divinylbenzene in the presence of anionic catalytic systems has been investigated [18] under different conditions. It was established that the cyclisation constant in anionic polymerisation is smaller than in the free-radical and cationic polymerisations. It is 2–4 mole litre^{-1} in free-radical polymerisation, 0.1–5 mole litre^{-1} in cationic polymerisation, and in most cases less than 1 mole litre^{-1} in anionic polymerisation.

The influence of solvent polarity, the nature of the alkali metal, and reaction temperature on the cyclisation constant has also been studied [18]. It follows from the experimental data that r_c increases with increasing solvent polarity in the sequence: tetrahydrofuran < ether < dioxan. The constant r_c in tetrahydrofuran varies with increasing temperature from 0.05 mole litre^{-1} at −78°C to 0.56 mole litre^{-1} at 20°C.

The nature of the solvent and the alkali metal (M) is known to influence the reactivity of the ion pair in anionic polymerisation. The uncyclised anion of *o*-divinylbenzene can exist as the free ion (VIII) and the ion pair (IX):



(VIII) (IX)

It was noted that the addition of $NaBPh_4$ to the polymerisation system lowers the reactivity of the ion pair and r_c. A free-anion propagation has therefore been suggested [18] for intramolecular cyclisation. As shown in Fig. 1, r_c diminishes also with increasing ionic radius of the counterion ($Li^+ > Na^+ > K^+$) in tetrahydrofuran; in dioxan the sequence based on the variation of r_c is reversed. It is suggested that the maximum degree of solvation of the Li^+ ion in tetrahydrofuran leads to the most reactive ion pair. In ether r_c diminishes in the sequence $K^+ > Li^+ > Na^+$. [18] The constant r_c in ether (dielectric constant $\epsilon = 4.3$ at 20°C) is intermediate between the value in tetrahydrofuran ($\epsilon = 7.4$ at 25°C) and in dioxan ($\epsilon = 2.2$ at 25°C).

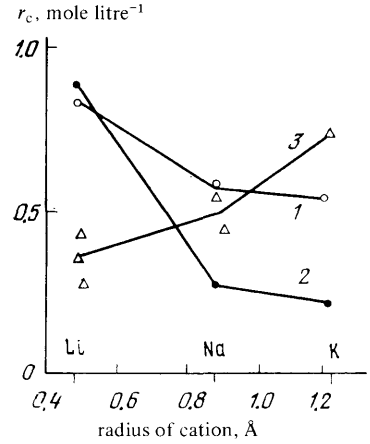


Figure 1. The effect of the counterion on the cyclisation constant of *o*-divinylbenzene in tetrahydrofuran: 1) at 20°C; 2) at 0°C; 3) the effect of the counterion on the cyclisation constant in dioxan at 20°C.

Thus one may conclude that the higher the reactivity of the growing ion pair, the greater the cyclisation constant.

The available data for the influence of the monomer structure on the rate of chain propagation refer mainly to the addition of free ions. The kinetics of many anionic polymerisation processes involving vinyl compounds in tetrahydrofuran with Na^+ as the counterion have now been investigated. The copolymerisation data are most important. Thus the following bimolecular rate constants have been obtained for the addition of a series of dienes to living polystyrylsodium in tetrahydrofuran at 25°C: [19]

Diene	$k_{1,2}$, litre mole^{-1} s^{-1}
Butadiene	32.7
Isoprene	17.0
2,3-Dimethylbutadiene	0.4 - 0.5

Such decrease of the rate can be explained both by the inductive effect of the methyl groups and by steric factors.

In the study of the copolymerisation of α- and β-methylstyrenes with "living" polystyrylsodium it was shown that both isomers are 40–50 times less reactive than styrene.

Steric hindrance is responsible for the very low reactivity of vinylmesitylene. In this case the breakdown of the coplanarity of the vinyl and phenyl groups lowers the reactivity of the monomer[20].

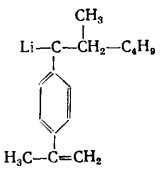
A detailed study of the relation between the structure of the monomer and its reactivity was carried out by Shima et al.[21]; the results are presented in Table 1.

Table 1. The rate constants $k_{1,2}$ for the addition of styrene derivatives to polystyrylsodium in tetrahydrofuran at 25°C.

Monomer	$k_{1,2}$, litre mole^{-1} s^{-1}
Vinylmesitylene	0.9
β-Methylstyrene	18.0
α-Methylstyrene	27.0
p-Methoxystyrene	50.0
p-t-Butylstyrene	110.0
2,4-Dimethylstyrene	160.0
p-Methylstyrene	180.0
o-Methylstyrene	320.0
Styrene	950.0

All the data examined above show that the addition of styrene derivatives to polystyrylsodium has a nucleophilic mechanism.

It might have been expected that the presence of the isopropenyl group in the *para*-position in *p*-DIPB would facilitate the addition of n-butyl-lithium to one of the two isopropenyl groups as a result of the increase in the length of the conjugated chain. However, the compound obtained is not capable of reacting further with n-butyl-lithium under the same conditions owing to the presence of an electron-donating substituent in the *para*-position relative to the isopropenyl group.



The reactivity of hydrocarbon monomers in anionic polymerisation processes has been studied mainly in relation to styrene, its derivatives and dienes. The determination of the characteristics of the anionic polymerisation of aromatic dialkenyl monomers is important for the determination of the relation between the reactivity of the active centres and their structure. The principal features of the anionic-coordination polymerisation of *p*-DIPB have been investigated[22]. The kinetic curves for the polymerisation of *p*-DIPB in benzene at 50°C at different *p*-DIPB and n-butyl-lithium (n-BuLi) concentrations are illustrated in Figs. 2 and 3. The study of the dependence of the rate of polymerisation of *p*-DIPB on the concentrations of the monomer and the initiator showed[22] that the rate of polymerisation is directly proportional to the monomer and initiator concentrations: $w = k[M][n\text{-BuLi}]$. The overall activation energy for this process in the temperature range 30–50°C is 15.3 ± 1.5 kcal mole^{-1}.

The chain propagation reaction under the influence of organolithium compounds is known to involve the interaction of the monomer molecules with an unassociated active centre[23,24].

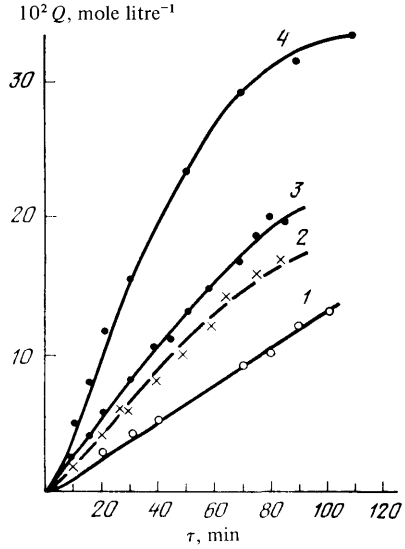


Figure 2. Kinetic curves for the polymerisation of *p*-DIPB under the influence of n-butyl-lithium in benzene at 50°C at different molar n-butyl-lithium concentrations: 1) 1.6×10^{-2}; 2) 3.5×10^{-2}, 3) 5.3×10^{-2}; 4) 8.4×10^{-2}; Q—the conversion of the monomer.

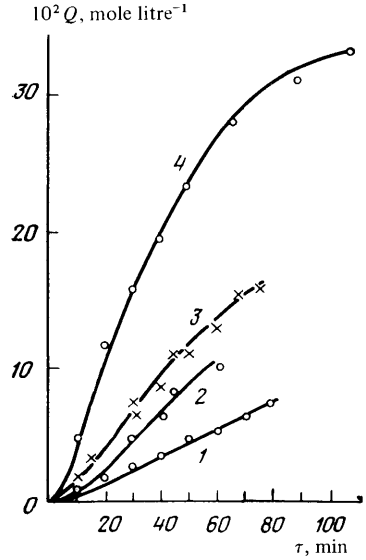


Figure 3. Kinetic curves for the polymerisation of *p*-DIPB under the influence of n-butyl-lithium in benzene at 50°C and different molar monomer concentrations: 1) 0.2; 2) 0.4; 3) 0.6; 4) 0.88.

It has been shown that the number of molecules in the associated species (n) and the stability of the latter increase in the sequence α-methylstyrene < isoprene < butadiene, i.e. the increase of the number and size of substituents in the carbanionic component of the active centre hinders association. Thus estimates by the kinetic method gave $n = 6$ for lithiopolybutadiene, 4 for polyisoprene, and 2 for polystyrene and poly-α-methylstyrene. The steric factors for p-DIPB fully inhibit association, as shown by the identical flow times of solutions of living and deactivated polymers at 50°C.[25]

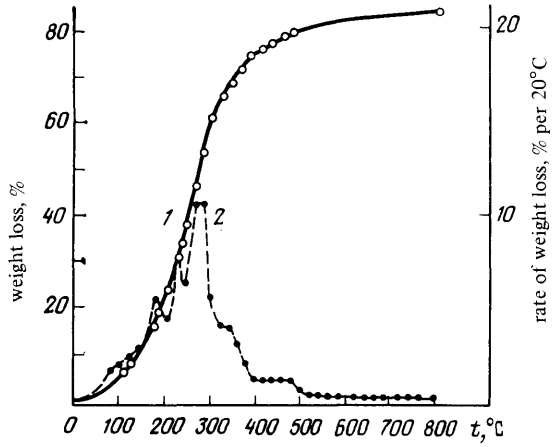


Figure 4. A gravimetric study of poly-p-DIPB in an atmosphere of argon: 1) weight loss (%); 2) rate of weight loss (% per 20°C).

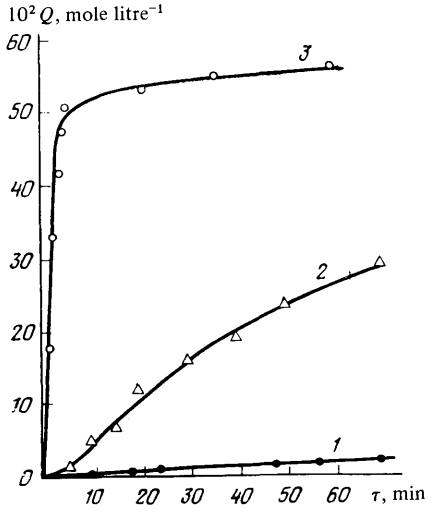


Figure 5. Kinetic curves for the polymerisation of α-methylstyrene (curve *1*), p-DIPB (curve *2*), and m-DIPB (curve *3*) in benzene.

The structure of poly-p-DIPB has been studied by infrared[26,27] and NMR spectroscopy[28]. It has been established on the basis of the changes in the intensity of the overtone C=CH_2 bond vibration band (1785 cm^{-1}), relative to the stretching vibration band (1620 cm^{-1}) characterising the vibration of the p-substituted benzene ring, that only one isopropenyl group is involved in the polymerisation of p-DIPB. The presence of the following structural elements has been established on the basis of the NMR spectra of the polymer: $CH_3-C\lesssim$ (chemical shift $\delta \simeq 0.4$ p.p.m.), $\gtrsim C-CH_2C\lesssim$ ($\delta = 1.4$ p.p.m.), $CH_3C=$ (two partly resolved peaks with $\delta = 2.05$ and 2.13 p.p.m.), CH_2 (several signals in the range $\delta = 5-5.4$ p.p.m.), and p-C_6H_4 (three peaks with $\delta = 6.6$, 6.9, and 7.2 p.p.m.).[28]

According to the results of thermomechanical analysis of poly-p-DIPB and the p-BIPB–butadiene copolymer, the glass point of poly-p-DIPB is 115°C and the yield point is 165°C; the glass point of the p-DIPB–butadiene copolymer is 41°C. A gravimetric study in an atmosphere of argon showed that the maximum extent of the main decomposition reaction of poly-p-DIPB is observed (on the basis of the overall weight loss of 88%) at 260–280°C (Fig. 4).[25]

In order to elucidate the influence of the second isopropenyl group on the polymerisation reaction under the influence of n-butyl-lithium, the authors[22] compared the reactivities of p-DIPB, m-DIPB, and α-methylstyrene. The kinetic curves for polymerisation in benzene (at 50°C) and in tetrahydrofuran (at 28°C), at monomer and initiator concentrations of 0.88 and 0.08 M respectively, established that the reactivities of the monomers decrease in the sequence m-DIPB > p-DIPB > α-methylstyrene[22,29] (Fig. 5).

Table 2. The electrical conductivities of solutions of "living" α-methylstyrene, p-DIPB, and m-DIPB polymers in tetrahydrofuran (cell constant 2.8×10^{-2} cm^{-1})*.

Solution	Resistance, Ω	κ, Ω^{-1} cm^{-1}	$10^{-3}\Lambda$, Ω^{-1} mole^{-1} cm^2
Poly-α-methylstyryl-lithium	$4.6 \cdot 10^5$	$6.0 \cdot 10^{-7}$	$7.1 \cdot 10^{-6}$
Poly-p-DIPB-lithium	$6.0 \cdot 10^4$	$4.7 \cdot 10^{-6}$	$5.6 \cdot 10^{-5}$
Poly-m-DIPB-lithium	$15.0 \cdot 10^3$	$1.9 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$

*Notation: κ is the specific conductance and Λ the molar conductance.

The high relative reactivities of m- and p-DIPB in the chain propagation steps in polymerisation in the presence of n-butyl-lithium can probably be explained by the decrease of the energy of interaction of the components of the ion pair due to steric factors (the branching of the carbanion). The experimental electrical conductivities of solutions of "living" polymers (Table 2) indicate an increase of the polarity of the lithium–carbon bond on passing from α-methylstyrene to p- and m-DIPB and show that the energy of the interaction of the components of the ion pair of the active centre decreases with increasing role of steric factors[25].

The electronic absorption spectra of "living" p- and m-DIPB polymers[25] (Table 3) showed that, when a more electron-donating solvent is used, the absorption maximum

undergoes a bathochromic shift and λ_{max} for poly-*p*-DIPB-Li, which is close to λ_{max} for 1,1-diphenylalkyllithium (428 μm), is evidently determined by the branching of the carbanion. With decrease of the stability of the associated species owing to steric hindrance, the relative content of the monomeric form increases and therefore at fairly high n-BuLi concentrations (10^{-3} M) there is a bathochromic shift of the absorption maximum on passing from benzene to tetrahydrofuran.

Table 3. The absorption spectra of "living" *p*- and *m*-DIPB polymers (25°C, n-BuLi concentration 10^{-3} M).

Monomer	Solvent	λ_{max}, nm
m-DIPB	benzene	335
m-DIPB	tetrahydrofuran	405
p-DIPB	benzene	424-425
p-DIPB	tetrahydrofuran	448-450

Table 4. The half-wave potentials (relative to the saturated calomel electrode).

Substance	$-E_{1/2}$, V	$I_c = i^*_{lim}/c$, A mole^{-1}
α-Methylstyrene	2.619	$2.3 \cdot 10^3$
p-DIPB	2.448; 2.691	$2.15 \cdot 10^3$, $2.9 \cdot 10^3$
m-DIPB	2.617	$4.6 \cdot 10^3$

*Notation: I_c is the specific current, i_{lim} the limiting current, and c the concentration of the given substance in solution.

Thus the characteristics of the propagation reaction and the nature of the structure of the active centres in the anionic polymerisation of aromatic dialkenyl monomers under the influence of n-butyl-lithium have been elucidated by kinetic, spectrophotometric, and conductimetric methods [27].

V. THE DILITHIUM CATALYST BASED ON *m*-DIISOPROPENYLBENZENE

In the polarographic determination of the electron affinities of α-methylstyrene, *p*-DIPB, and *m*-DIPB, (Table 4) it was found [29] that the addition of electrons to the isopropenyl groups in *m*-DIPB takes place independently; in *p*-DIPB the influence of the isopropenyl groups is manifested by the formation of two separate waves and a considerable displacement of the value of $E_{1/2}$ for the first wave relative to that for α-methylstyrene. Consequently n-butyl-lithium can add to the two isopropenyl groups in *m*-DIPB. This phenomenon, which was previously unknown for the given class of compounds, has been used to obtain dilithium catalysts based on *m*-DIPB. [29] The 890–900 cm^{-1} band was found to be missing from the infrared spectrum of the product of the carboxylation of dilithio-*m*-diisohexenylbenzene, which indicates the simultaneous addition of n-butyl-lithium to the two isopropenyl groups. The 1,3-disubstitution of the ring is responsible for the appearance of bands at 720 and 805 cm^{-1}; the 860 cm^{-1} band refers to the vibrations of the C=O group of the carboxyl. The results of the elemental analysis of this compound are in good agreement with the calculated values [29].

The molecular weight of polystyrene (W), determined from the intrinsic viscosities, was consistent with the relation [30]

$$W = 2M/N,$$

where M is the amount (in grams) of the polymerised monomer and N is the number of moles of catalyst which have been consumed. Consequently the active centres are dianions. The activity of the dilithium catalyst based on *m*-DIPB in the polymerisation of styrene is close to that of s-butyl-lithium (Fig. 6).

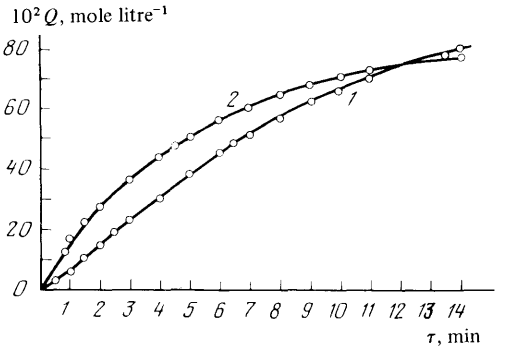


Figure 6. Kinetic curves for the polymerisation of styrene in the presence of dilithio-*m*-diisohexenylbenzene (curve *1*) and *s*-butyl-lithium (curve *2*) at 40°C; lithium concentration 3×10^{-3} M; styrene concentration 1 M; solvent—benzene.

The use of organodilithium compounds leads to extensive possibilities for the synthesis of ternary block copolymers of the type ABA and oligomers with terminal functional groups [31–36]. The previously known dilithium polymerisation initiators are largely insoluble in hydrocarbons or require the use of a homogenising comonomer, are frequently unstable, and require prolonged preparation.

Disodio, dilithio-, and dirubidio-α-methylstyrene tetramers, formed in the reaction between the alkali metal and a solution of α-methylstyrene in electron-donating media, have been described in the literature [34,35].

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Thus the literature data examined in the present paper review and their analysis reveal the considerable possibilities for the employment of aromatic dialkenyl compounds in macromolecular chemistry.

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The Sedimentation of Polydisperse Polymers

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The most important problems in the sedimentation of one component of two-component mixtures and polydisperse polymers have been discussed. Particular attention has been paid to the application of theory in the treatment of sedimentation data. It has been shown that to calculate the molecular mass distribution (MMD) from sedimentation diagrams of polydisperse polymers, the best theory is that based on the Trautman relationships describing the Johnston-Ogston effect for the case of a binary mixture, the concept of local concentration, and the principle of additivity of the paired interactions of the components of the mixture. Allowance for the diffusion broadening of the curves is made using Fujita's theory by means of model functions. The distribution with respect to the sedimentation coefficients (or the MMD) is calculated by means of a computer from one recording. The bibliography contains 99 references.

CONTENTS

I.	Introduction	699
II.	Sedimentation of one component	699
III.	Sedimentation of two components	701
IV.	Sedimentation of polydisperse polymers	702
V.	Conclusion	711

I. INTRODUCTION

One of the chief methods for determining the molecular mass distribution (MMD) of synthetic polymers is by the velocity sedimentation of polymer solutions in the ultracentrifuge[1-4].

The theoretical principles of the method of velocity sedimentation were formulated at an early date[5], various aspects of the application of the method to specific systems have been dealt with in many reviews and monographs[2-15], and the construction of ultracentrifuges is being improved[15-17]. Nevertheless, velocity sedimentation has not found extensive application in research by synthetic chemists. Both theoretical problems in the analysis of polymerisation mechanisms[18] and technical problems in modelling synthesis processes and the selection of reactor design[19,20] require rapid determination of the MMD. The generally adopted extrapolation method[2-6] for finding the MMD is too cumbersome and tedious, however, and the single-concentration and single-recording approximations[3,21-26] have insufficient theoretical foundation. The method of equilibrium sedimentation in an ideal solvent, which has good theoretical basis[2-7,11-15], is not used in practice to determine the MMD of polydisperse polymers. This method is inconvenient chiefly because it is necessary to carry out the ultracentrifuging of the polymer solutions for a long period (several days).

The form of the boundary in the sedimentation of a polydisperse polymer depends not only on the non-uniformity of the specimen but also on a number of other factors: the hydrostatic pressure, diffusion, the concentration dependence of the sedimentation coefficients S, the sector form of the cell, and the cross-term hydrodynamic interactions of the components—the Johnston-Ogston effect (JOE).[3,13,14,27-29] In spite of some progress in the understanding of the nature of these effects, there is no simple and reliable method which makes it possible to take account of all the factors influencing the form of the sedimentation boundary. It is obviously appropriate to raise the question of the influence of a given factor on the form of the sedimentation distributions, their dependence on the properties of the polymer-solvent system, the average molecular masses, the polydispersity, and the type of MMD curve. In particular, neither the hydrodynamic[30-32] nor the thermodynamic[33-35] aspects of the influence of the hydrostatic compression of the solvent on the sedimentation and flotation (negative sedimentation)[36-42] of solutions of polydisperse polymers have been fully studied.

The present review examines the sedimentation of one- and two-component† systems and polydisperse synthetic polymers, except for the special problems of the sedimentation of biological materials[7]. In the examination of the first two problems, only some fundamental questions will be dealt with.

II. SEDIMENTATION OF ONE COMPONENT

Velocity sedimentation gives directly the distribution $g(S_0)$ (S_0 is the sedimentation constant) of a polydisperse polymer. The molecular mass distribution $g(M)$ (M is the molecular mass) is then found from the equations

$$S_0 = K_S M^\gamma, \quad M = (S_0/K_S)^{1/\gamma}; \tag{1}$$

$$g(M) = \gamma S_0 g(S_0)/M, \tag{2}$$

where K_S and γ are constants for a series of polymer homologues in a given solvent. It can be seen that to determine the MMD from Eqns. (1) and (2) it is necessary to find both the sedimentation constants and the absolute molecular masses of the polymer fractions (preferably narrow).

The study of the sedimentation of the fractions is of not only practical but also theoretical interest (for the comparison of the results with conclusions reached from theory)[13,14]. To anticipate slightly, it may be noted that it is only for the sedimentation of one component that a rigorous theoretical approach has been developed[13,14] and

† Here and subsequently, reference is made to hydrodynamic and not thermodynamic components, that is the solvent is regarded not as a component but as the medium.

the molecular parameters of the solute and the solvent used to calculate the time dependence of the radial distribution of the concentration in the cell[13,14,43-49].

Polymers in all solvents, including thermodynamically ideal, are characterised by the following concentration dependence of the sedimentation coefficients:

$$S=S_0/(1+kc), \tag{3}$$

where S is the sedimentation coefficient of the component (fraction), c the concentration, and the coefficient k characterises the hydrodynamic interactions of identical macromolecules (which also depend on the thermodynamic properties of the system). A theoretical interpretation of the parameter k has been given[50,51], and in the study of fractions, extensive experimental material has been accumulated on the relationship between k and the characteristics of the polymer chains[3,36,52-62].

The influence of pressure P on the sedimentation coefficients is taken into account by means of the parameter μ:[2-15,43-49,53,63,64]

$$S^P=S^1/(1+\mu P), \tag{4}$$

or

$$S^P\approx S^1(1-\mu P), \tag{4a}$$

where S^P and S^1 are the sedimentation coefficients at pressures P and 1 atm respectively. It can be seen that Eqn. (4a) is a particular case of the more general equation (4), but before the work of Jones and coworkers[44-48], the theoretical analysis of sedimentation processes was based on Eqn. (4a). Eqns. (4) and (4a) lead to the following equations:

$$S^P=S^1/[1+m(r-1)],\ r=(x/x_0)^2; \tag{5}$$

$$S^P=S^1[1-m(r-1)]; \tag{5a}$$

$$m=\frac{1}{2}\mu\rho_0 x_0^2\omega^2, \tag{6}$$

where x and x_0 are the running coordinate and the coordinate of the meniscus respectively, ρ_0 the density of the solvent, and ω the angular rate of rotation of the rotor of the ultracentrifuge.

With allowance for the concentration dependence of the sedimentation coefficient, the influence of pressure and diffusion, and also the sector form of the cell, the equation for the ultracentrifuge was solved[48] by a numerical method, that is the time dependence of the radial distribution of the concentration and the concentration gradient was calculated. These calculated characteristics show good agreement with the experimentally observed relationships. It is usually necessary, however, to solve the inverse problem—to find the molecular parameters from experimental data. It was found that any analytical expressions describing sedimentation in terms of the coordinate of the boundary and time are approximate. The relative error between the exact (numerical) and approximate (analytical) solutions is 3% for S_0 and 12% for m. The theory[48] does not take account of the reflection of macromolecules from the meniscus[13,14] or the pressure dependence of the diffusion coefficient[49]. Moreover, in the analysis of experimental data, the correction for dispersal should not be forgotten[21,65,66]. In view of the approximate nature of the simple analytical expressions, it has been suggested[48] that the variable coordinate of the meniscus be used in calculations in the treatment of experimental data.

In spite of these unsatisfactory features, the theory[48] marks an important stage in the development of velocity sedimentation and makes it possible to interpret reliably the experimental data on the sedimentation of fractions of synthetic polymers. The most important conclusions from this work are examined below.

1. In agreement with experimental data[30,67], in the sedimentation of one component, there is produced a plateau region in which there is no concentration gradient.

2. The concentration in the range of the plateau (c_a) is given by the expression

$$c_a=c_0[1+m(r-1)]/r, \tag{7}$$

where c_0 is the initial concentration. Thus the simple dilution law $c_a = c_0/r$ is realised only in the limit as $m \to 0$. For $m = 1$, there is not change in concentration with time in the range of the plateau: $c_a(t) = c_0$; a value $m < 1$ corresponds to dilution, and $m > 1$ corresponds to concentration in the sedimentation process.

3. The determination of the position of the boundary from the second moment of the distribution of the displacements[3,13,21,43,53,65,68] is justified only for the limiting case[69] ($m = 0$, $c_a = c_0/r$) of the sedimentation of one component.

4. The following equation is proposed[48] for the determination of S_0 and m

$$\ln r/(2\omega^2 t)=B/2\omega^2 t+E+H\cdot 2\omega^2 t,$$

where t is the time, and B, E, and H are constants which are found by the least squares method. The constant B corresponds to the displacement of the meniscus (by not more than 1.2 mm), and can apparently partly compensate the effects of reflection from the meniscus and the displacement of the actual start of sedimentation. If the constants E and H are calculated, S_0 and m can be determined from the equations:

$$S_0=(1+\alpha)E,\ \alpha=kc_0;$$

$$m=[1/(2\alpha+1)]\cdot\left[\alpha-\frac{(1+\alpha)H}{E^2}\right].$$

5. Fujita's equation[13,14,43] has been widely used in the treatment of experimental data

$$S=\ln r[1-R(r-1)]/2\omega^2 t\ \ R=-\frac{m}{2}+\left(\frac{1-m}{2}\right)\frac{kc_0}{1+kc_0} \tag{8}$$

and is applicable for small values of m.

6. The fact that $\ln x$ or $\ln r$ are linearly dependent on t does not indicate that the effects of compression and dilution are compensated, just as extrapolation to the meniscus does not guarantee that complete allowance has been made for the influence of pressure. As already noted, this is due to the inadequacy of the simple analytical expressions for the actual sedimentation of a polymer fraction, characterised by a definite polydispersity.

7. In a number of cases[21,59,60,70], an increase in the coefficient k with increase in the angular rate of rotation of the centrifuge rotor ω has been detected. This effect is usually related to an increase, with increase in ω, in the average concentration in the region of the plateau, corresponding to the experimental range of change in the coordinate x; this leads to a decrease in S and hence to an increase in k. It is not accidental that with decrease in the molecular mass, the magnitude of this effect decreases.

8. The scatter in the values of m or μ determined by different methods[26] or even by the same method[21] is due both to the approximate nature of the original analytical

expressions and to the fact that these parameters are determined from small changes in the sedimentation coefficients.

III. SEDIMENTATION OF TWO COMPONENTS

The sedimentation of two macromolecular components is accompanied by cross-term hydrodynamic interactions, leading to an increase in c and a decrease in S for the slow component, and to a decrease in c and an increase in S for the fast component. Some experimental data[71] on the Johnston–Ogston effect will be examined.

Table 1. Characteristics of PαMS specimens[71].

Specimen	10^{-6} M	S_0, Svedberg units	k, dl g^{-1}	Solvent
A–S	0.73	13.89	0.489	cyclohexane
A–F	1.52	19.47	0.648	cyclohexane
B	0.46	11.37	1.98	toluene
C	1.38	17.78	4.01	toluene



Figure 1. Sedimentation diagram for a mixture of specimens A–S and A–F PαMS in cyclohexane: $c_0 = 0.316$ g dl^{-1}, 35°, $\omega = 59\,780$ r.p.m.

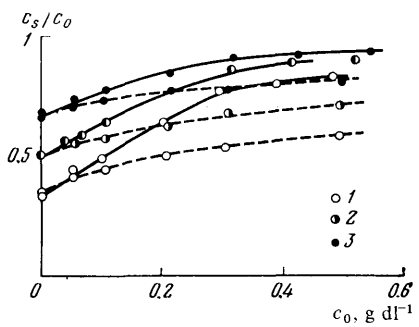


Figure 2. Dependence of the apparent relative concentration of the slow component of PαMS on the total initial concentration. The broken lines correspond to a mixture of specimens A–S and A–F in cyclohexane: *1*) $c_F^0/c_S^0 = 1.848$; *2*) 1.00; *3*) 0.478. The continuous lines give the data for a mixture of specimens B and C in toluene: *1*) $c_F^0/c_S^0 = 1.957$; *2*) 1.00; *3*) 0.498.

Fig. 1 gives the sedimentation diagram of a specimen A of poly-α-methylstyrene (PαMS) in cyclohexane (CH) at 35° (close to the θ-point). This specimen was obtained by anionic polymerisation[72] with the simultaneous use of mono- and bifunctional initiators, and is practically a mixture (1 : 1) of two specimens A–S and A–F (see Table 1). It can be seen that there is a marked difference in the areas under the peaks, although the original concentrations of the components are identical. Similar sedimentation diagrams were obtained for mixtures of specimens B and C. Fig. 2 gives the dependence of the apparent relative concentrations of the slow component of PαMS on the total initial concentration. The Johnston–Ogston effect (the increase in the concentration of the slow component) is clearly observed in both toluene and cyclohexane, but the effect is much greater in the thermodynamically good solvent (toluene) than in the ideal solvent (cyclohexane).

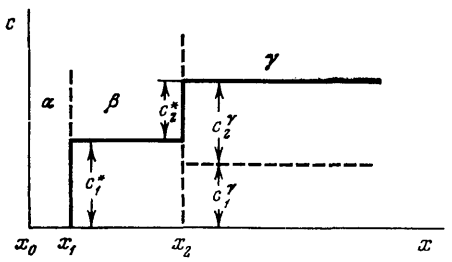


Figure 3. Schematic representation of the dependence of the concentration c on the coordinate x in the cell of the ultracentrifuge in the sedimentation of a two-component mixture.

A theory of the effect has been given[29] on the basis of the ideas of Johnston and Ogston[27]. The sedimentation of a two-component mixture can be considered; the slow component is denoted by the index 1, and the fast component by the index 2; the sedimentation constants of the components are S_{01} and S_{02} respectively, and $S_{02} > S_{01}$. At some moment of time in the cell of the ultracentrifuge, the dependence of the total concentration c on the coordinate x has the form shown in Fig. 3 (if the influence of diffusion is neglected). Here and subsequently it is assumed that the increments in the refractive indices of the components are identical, and that any optical system of the centrifuge can be used to determine this relationship. The α-region corresponds to the pure solvent, the β-region corresponds to the sedimentation of component 1, and in the region of the γ-plateau, movement of both components takes place (Fig. 3). The concentrations c_1^* and c_2^* are recorded directly. The expressions

$$p_i = c_i^* r_i / c_i^0, \quad i = 1, 2, \tag{9}$$

where c_i^0 is the concentration of the component i in the original solution, are compiled. If the correction for pressure is small, and the sedimentation of one component does not influence the sedimentation of the other, then $p_i = 1$. It has been shown experimentally, however, that in all cases $p_1 > 1$, and $p_2 < 1$ [7,14,27–29,71] (see Fig. 2).

The experimentally observed picture of the movement of the components of the mixture is as follows. At the initial moment of time, the slow first component "remains in its position", since for this component the medium containing the fast (high-molecular-weight) second component represents a medium with an increased hydrodynamic resistance, whereas for the second component, the first (low-molecular-weight) component represents a medium with a lowered hydrodynamic resistance. In the region left by the fast component, there is a relative increase in the rate of movement of the slow component; the moving boundary then acts as a kind of "dam", and the concentration of the first component increases, leading to a relative decrease in the concentration of the second component. Thus the physical factor responsible for the JOE is the increase (fast) or decrease (slow) in the rate of movement of one component in the presence of the other.

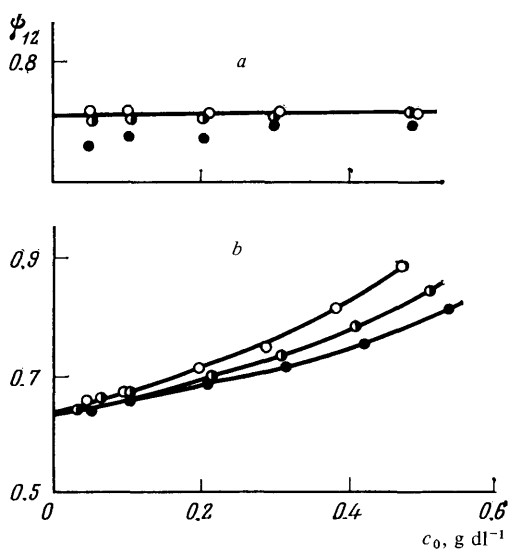


Figure 4. Concentration dependence of ψ_{12}: the symbols are the same as in Fig. 2; solvents: *a*) CH, *b*) toluene; the points of intersection of the curves with the ordinate correspond to the values $S_S^0/S_F^0 = S_{01}/S_{02}$.

In the theory of Trautman and coworkers[29], the changes in the concentrations of the components are taken into account by means of the parameter ψ_{12} (see Fig. 3):

$$c_1^\gamma/c_1^0 = (x_0/x_2)^{2\psi_{12}} = r_2^{-\psi_{12}}, \tag{10}$$

where the index γ refers to the values of the quantities in the region of the γ-plateau. It can be shown that the value of ψ_{12} is determined by the difference in the values of the sedimentation coefficients of the first and second components in the region of the γ-plateau:

$$\psi_{12} = \int_0^t S_1^\gamma \,dt \Big/ \int_0^t S_2^\gamma \,dt. \tag{11}$$

The experimental data[71] indicate that the concentration dependence of the sedimentation coefficients of the components of the mixture satisfies the relationship

$$S_i = S_{0i}/(1 + k_i c_i + k_{ji} c_j), \tag{12}$$

where the coefficient k_{ji} reflects the influence of the jth component on the sedimentation of the ith component. In a θ-solvent (CH for PαMS), $k_{ji} = k_i$, but in a good solvent, only the approximate relationship $k_{ji} \simeq k_i$ holds. Application of Eqn. (12) to the sedimentation of the components in the region of the γ-plateau gives:

$$\psi_{12} = S_{01}/S_{02}. \tag{13}$$

The original concentrations of the components c_1^0 and c_2^0 are related to the parameter ψ_{12} as follows:

$$c_1^0 = c_1^* (r_2 - r_1)/[r_2^{1-\psi_{12}} - 1], \tag{14a}$$

$$c_2^0 = c_1^* r_1 + c_2^* r_2 - c_1^0. \tag{14b}$$

By measuring the areas under the peaks c_i^* (see Fig. 1), it is possible to use Eqns. (14a) and (14b) to determine the parameter ψ_{12}. Fig. 4 gives the concentration dependence of this parameter[71]. For the θ-system PαMS–CH, relationship (13) is fulfilled, whereas in a good solvent (toluene), the value of ψ_{12} increases with increase in concentration.

Undoubtedly, the most important feature is that in the limit, as $c \to 0$, the parameter ψ_{12} does not tend to unity, which would correspond to the widely held view that the JOE decreases with decrease in the concentrations of the components, but becomes equal to the limiting value corresponding to Eqn. (13) in the case of the PS–CH system, or approaches it in the case of the PS–toluene system (PS = polystyrene). This in turn leads to the important conclusion that it is impossible to eliminate the influence of the Johnston–Ogston effect by extrapolating the experimental data to zero concentration.

If the influence of hydrostatic pressure is taken into account from the generalised dilution law (7), the following equations are obtained instead of Eqns. (14a) and (14b):

$$c_1^0 = c_1^* (y_2 - y_1)/[y_2^{1-\psi_{12}} - 1];\ y_i = r_i/[1 + m(r_i - 1)]; \tag{15a}$$

$$c_2^0 = c_1^* y_1 + c_2^* y_2 - c_1^0. \tag{15b}$$

IV. SEDIMENTATION OF POLYDISPERSE POLYMERS

1. CHARACTERISTICS OF THE EXTRAPOLATION METHOD

The graphical–analytical procedure widely adopted at present[2-4] for determining the distribution curves with respect to sedimentation coefficients (and also the MMD) of polymers is based on the assumption of simple additivity of the movement of the components and the factors operating in the system. It is assumed that the effects of pressure, diffusion, and the concentration dependence of the sedimentation coefficients are independent and additive and can be considered in turn. The apparent distributions $g^*(S, t)$, not corrected for diffusion broadening, are calculated from Eqns. (5), (5a), and (6) and the relationship

$$g^*(S, t) = zrx/[1 + m(r-1)]^2, \tag{16}$$

where the displacement $z \sim dc/dx$. Extrapolation of the $g^*(S, t)$ curves for a number of concentrations to infinite time (that is $1/t \to 0$) eliminates the diffusion factor, after

which the $g(S)$ distributions are extrapolated to zero concentration, which makes it possible to take account of the $S(c)$ relationship. It is assumed that these extrapolations simultaneously eliminate the influence of cross-term interactions; as shown in the previous section, however, the JOE cannot be eliminated by extrapolating the data to zero concentration. It is apparently not accidental that research experience[23] shows that there are considerable complications in carrying out the extrapolations. Moreover, the final distribution loses "fine" details (small or poorly resolved maxima, a "tail"), and are too narrow.

It is possible to distinguish three types of polymer, differing from one another in the width of the distribution curves $g(S)$: 1) highly polydisperse polymers contain high-molecular-weight fractions (a "tail"), which reach the foot of the cell, whereas the low-molecular-weight components do not leave the meniscus; 2) for polymers of medium polydispersity, the boundary occupies almost the entire column of solution, that is the boundary leaves the meniscus, but the "tail" of the distribution does not reach the foot; and 3) the boundary for weakly polydisperse polymers occupies approximately half (or less) of the height of the column of solution in the cell.

This division is of course to some extent arbitrary, since a given specimen in a thermodynamically ideal solvent and in a good solvent, or with a considerable variation in concentration, may correspond to different types of polydispersity with respect to $g(S)$. As will be shown subsequently, however, polymers of the second and third types differ considerably from one another in the relative roles of diffusion and the JOE. The sedimentation of highly polydisperse polymers (the first type) has already been examined[37].

The practical realisation of the extrapolation of distributions sometimes encounters difficulties even in making allowance for diffusion[23,73]. Thus the sedimentation of an industrial specimen of polystyrene (its characteristics will be given below) at $c \leq 0.3$ g dl^{-1} gives $g^*(S, t)$ curves which do not change in the same sense, and the height at the distribution maximum decreases with time. The introduction, with fairly crude assumptions, of corrections for dilution leads to $g^*(S, t)$ distributions for which the ordinates at the maximum increase with increase in t, and it is possible to eliminate the influence of diffusion[73]. The example given illustrates a characteristic unsatisfactory feature of calculations using Eqns. (5), (5a), (6), and (16)—the neglect of sector dilution. For a polymer which is non-uniform with respect to mass, this problem is not so simple, since different components of the mixture are diluted in different ways, both from purely geometric considerations and because they are situated in regions with different local concentrations.

Another unsatisfactory feature of the above widely adopted method of treating sedimentation diagrams is that the treatment is implicitly based on the concept of plateau concentration. In fact, all polymers are characterised by a $S = S(c)$ relationship, so that it is possible to relate a distribution $g^*(S, t)$ to a specific concentration c without additional corrections only if the concentration remains unchanged during sedimentation. The concentration remains practically unchanged in the region of the plateau, whereas along the boundary it increases from zero to the plateau concentration. Thus Eqns. (5), (5a), (6), and (16) are inseparable from the assumption that a decisive role in the sedimentation of a polydisperse polymer is played by the concentration in the region of the plateau. This concept is directly contradicted by the above results of the study of the sedimentation of two-component systems. This leads to the consideration of another fundamental problem.

On the basis of Fujita's equation (8),[13,14] relationships have been obtained[74] for calculating $g^*(S, t)$ with allowance for the $S(t)$ relationship and the change in the concentration along the boundary. Fig. 5 gives the $g^*(S, t)$ curves for a polystyrene specimen PS-1 (data on this specimen are given below) in CH at 34°C, calculated from the published equations[74]. The distributions with respect to sedimentation coefficients change in different senses to such an extent that it is not possible to eliminate diffusion broadening. The error in this case[74] is that for the intermediate range, the simple concentration c is used throughout, with no indication of its constituent components.

2. ROLE OF THE DIFFUSION FACTOR IN THE SEDIMENTATION OF POLYDISPERSE POLYMERS

a) The use of Fujita's theory[75] to estimate the diffusion broadening of the boundary

Allowance for diffusion broadening of the boundary is usually made[2-4] for each concentration with extrapolation of the distributions $g^*(S, t)$ or $G^*(S, t)$ (where $G^*(S, t)$ is the integral curve) to infinite time (that is $1/t = 0$). It is necessary, however, not only to eliminate the diffusion broadening of the distributions but also to determine quantitatively the role of diffusion and to determine the dependence of the diffusion factor on the molecular mass, polydispersity, and nature of the MMD curves of the polymers. This last feature is important in itself, and also in the development of single-point (single-recording) methods for calculating the MMD of polymers.

Fujita's theory[14,75] makes it possible to determine the role of diffusion in the sedimentation of polydisperse polymers[26,66,76]. This theory examines the sedimentation, in an "ideal sedimentation solvent"[14] in a rectangular cell, of a polymer of medium or low polydispersity, which does not contain appreciable quantities of low-molecular-weight fractions, that is $g(S)|_{x=x_0} = g'(S)|_{x=x_0} = 0$, and which does not contain high-molecular-weight fractions, that is a distribution "tail" which rapidly reaches the foot of the cell. Thermodynamically ideal behaviour is included as a necessary condition in the concept of an "ideal sedimentation solvent". Another important condition is the absence of all hydrodynamic interactions or the absence of concentration dependences $S(c)$ and $D(c)$ (D is the diffusion coefficient) and cross-term interactions. In addition, the following approximate relationship is used:

$$x - x_0 = x_0\omega^2 tS.$$

Since the sedimentation is ideal, the parameter K is constant:

$$K = SD = S_0D_0 = \text{const.} \qquad (17)$$

Subsequently, the interpretation of the experimental data will be related chiefly to this parameter. Using familiar relationships[3], it is possible to express K in terms of molecular parameters

$$K_0 = S_0D_0 = \frac{RT(1-\bar{v}\rho_0)}{N_A^2P^2\eta_0^2}\left(\frac{M}{\bar{h}_0^2}\right) = K_0^{\text{theor}}, \qquad (18)$$

where R is the universal gas constant, T the temperature, N_A Avogadro's number, P the frictional constant ($P = 5.1$

was used in the calculations), η_0 the viscosity of the solvent, $\overline{h_0^2}$ the dimensions of the coiled molecule in the ideal solvent, and $\overline{v}$ the partial specific volume of the polymer.

Despite these restrictions, Fujita's theory was the first to deal simultaneously with the sedimentation and diffusion of polymers of medium polydispersity, since Gosting's relationships[77] were derived with the condition that D = const for all components, that is, strictly speaking, for polymers (fractions) with low polydispersity. Analysis of the published expressions[66] for the dispersion of the displacements $\overline{\xi}^2$ from the theories of Fujita and Gosting shows that they are identical, but the former theory has the advantage of being general. Fujita's theory shows that Gosting's relationships are also inapplicable to the sedimentation of polymers of medium polydispersity if the weighted-mean diffusion coefficient is used. After allowance for the effect of self-contraction, the experimental data[66,78,79] on the dependence of $\overline{\xi}^2$ on t show qualitative agreement with theory.

Table 2. Characteristics of the systems studied*.

No.	Polymer	Conditions of synthesis	Solvent for the sedimentation; temperature, °C	Density of solvent ρ_0, g ml^{-1}	$10^9\mu$	$10^{15}K_S$	ν	$10^{-5}\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1	PS	laboratory (high-weight fraction (Ref.80))	CH; 34°	0.7670	1.6	1.5	0.50[21]	10.8	1.70
2	PS	industrial	CH; 34°	0.7670	1.6	1.5	0.50[21]	2.25	2.27
3	PVA	laboratory (Ref.81)	BEK; 29°	0.8183	1.5	6.03	0.44[**82]	13.6	2.01
4	PVA	laboratory (Ref.81)	BEK; 29°	0.8183	1.5	6.03	0.44[**82]	5.19	1.78
5	PPhIA	polycondensation in solution (Ref.83)	DMF—0.25% LiCl; 25°	0.9474	4.0	2.8	0.39[84]	3.33	1.48
6	PPhIA	polycondensation in solution (Ref.83)	DMF—0.25% LiCl; 25°	0.9474	4.0	2.8	0.39[84]	2.04	1.85
7	PPhIA	polycondensation in solution (Ref.83)	DMF—0.25% LiCl; 25°	0.9474	4.0	2.8	0.39[84]	1.27	2.29
8	PAN	industrial	DMF—THF (1 : 1)	0.9165	1.7	2.0	0.43	2.12	2.15
9	PVC	industrial	THF; 25°	0.8880	0	9.87	0.35[85]	0.89	2.06

*Abbreviations: PS = polystyrene, PVA = polyvinyl acetate, PPhIA = poly(*m*-phenylene)isophthalamide, PAN = polyacrylonitrile, PVC = polyvinyl chloride, BEK = butyl ethyl ketone, DMF = dimethylformamide, THF = tetrahydrofuran.
**The equation is applicable for a concentration of 0.4 g dl^{-1}.

As noted above, allowance for the diffusion broadening of the boundary for polydisperse polymers is made difficult by the fact that the distributions $g^*(S, t)$ do not change in the same sense (see Fig. 5). By modifying slightly the correction for dilution[73], it is possible to improve considerably the extent to which the $g^*(S, t)$ curves change in the same sense and to carry out the extrapolation to $1/t = 0$ for specimens of PS and polyvinyl acetate (PVA) (see Table 2). For polymers with a low polydispersity—poly(*m*-phenylene)isophthalamide (PPhIA), polyacrylonitrile (PAN), and polyvinyl chloride (PVC)—calculation using Eqn. (5), (6a), (6), and (16) gave distributions $g^*(S, t)$ which changed satisfactorily in the same sence[76].

The asymptotic solution of the equation describing the broadening of the boundary in the sedimentation of a polydisperse substance has the following form[75]:

$$g^*(S, t) = g(S) - \frac{1}{4\tau}\frac{d}{dS}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right] - \ldots ; \quad (19)$$

$$G^*(S, t) = G(S) - \frac{1}{4\tau}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right] - \ldots ; \quad (20)$$

$$\tau = \omega^2 x_0^2 t/4K. \quad (21)$$

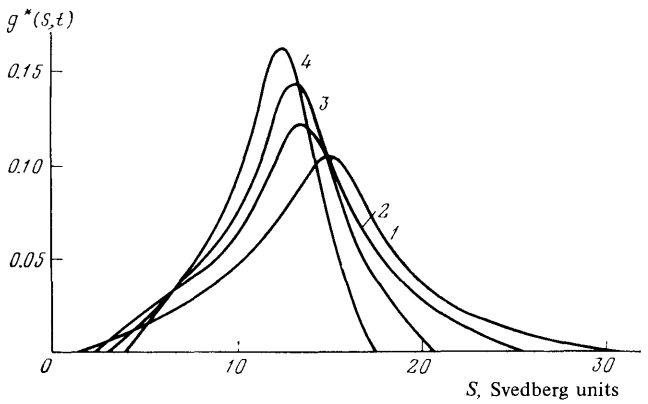


Figure 5. Normalised $g^*(S, t)$ curves for the specimen PS-1 (c = 0.3016 g dl^{-1}, ω = 40 000 r.p.m.), calculated from published equations[74]; time, s: *1*) 887, *2*) 1487, *3*) 2387, *4*) 3287.

In accordance with Eqn. (20), by plotting the sedimentation coefficients S^* against $1/t$ for constant G, it is possible from the magnitude of the intercept to find the values of $S = S^*_{t=\infty}$, and finally to obtain the distribution $G(S)$ corrected with allowance for diffusion.

The time dependence of S^* at constant G^* is given by the equation

$$S^* = a_0 + a_1/\tau + \ldots ; \quad (22)$$

$$a_0 = S, \; a_1 = \frac{1}{4}\left[\frac{1}{S^2} - \frac{g'(S)}{Sg(S)}\right]. \quad (22a)$$

The slope of this relationship $Y(S)$ is given by[75]:

$$Y(S) = -\left[\frac{K}{\omega^4 x_0^2 g(S)}\right]\frac{d}{dS}\left[\frac{g(S)}{S}\right]. \quad (23)$$

Since $dG = g(S)dS$,

$$\int_{G^0}^{1} Y(S)\,dS = \Xi = \frac{K}{\omega^4 x_0^2}\left[\frac{g(S^0)}{S^0}\right], \quad (24)$$

where Ξ is the area under the plot of Y against G, and the quantities G^0, $g(S^0)$, and S^0 correspond to the value $Y(S^0) = 0$. Thus K can be calculated from the experimentally determined values of Ξ, $g(S^0)$, and S^0 using Eqn. (24).

If the $g^*(S, t)$ distributions are extrapolated, it is possible to determine K as follows[86]. The slope $W(S)$ of the plot of $g^*(S, t)$ against $1/t$ for constant S, in accordance with Eqn. (19), is given by

$$W(S) = -\frac{K}{\omega^4 x_0^2}\frac{d}{dS}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right]. \quad (25)$$

Integration of this expression with respect to S gives the basic relationship for determining K:

$$\int_{S_A}^{S_B} W(S)\,dS = -\frac{K}{\omega^4 x_0^2}\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right]_{S_A}^{S_B}. \quad (26)$$

The limits of integration S_A and S_B correspond to the value $Y(S_{A,B}) = 0$. For a Gaussian function, that is for

$$g(S) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left\{-\frac{(S-S_m)^2}{2\sigma^2}\right\}, \quad (27)$$

the values of $S_{A,B}$ are found from the obvious condition $g^*(S_{A,B}) = g(S_{A,B})$, which leads to the following equation:

$$\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(S-S_m)^2}{2\sigma^2}\right]_{S_A}^{S_B} = \frac{1}{\sigma^*\sqrt{2\pi}}\exp\left[-\frac{(S-S_m)^2}{2(\sigma^*)^2}\right]_{S_A}^{S_B},$$

where $\sigma^* = \sigma + \Delta\sigma$ is the dispersion of the distribution $g^*(S, t)$. If it is assumed that $\Delta\sigma \ll \sigma$, then

$$S_{A,B} = S_m \pm \sigma, \quad (28)$$

$$\left[\frac{g(S)}{S^2} - \frac{g'(S)}{S}\right]_{S_m-\sigma}^{S_m+\sigma} = \frac{2S_m(S_m^2 - 3\sigma^2)}{\sqrt{2\pi e}\,\sigma^2(S_m^2-\sigma^2)^2}. \quad (29)$$

The value of the integral in the left-hand side of Eqn. (26) is determined from experimental data, so that K can be calculated from Eqns. (26) and (29). If the $g^*(S, t)$ curves are symmetrical and similar to a Gaussian distribution function, and if there is no removal of the distributions from the meniscus, it is better to use this method for determining K.[86]

Both methods for determining K have been verified using a large amount of experimental material; thus the calculations for all concentrations of the systems PS–CH and PPhIA–DMF–0.25% LiCl have been duplicated. Since the two methods gave practically identical results, the values of K are subsequently given without an indication of the method of determination. Fig. 6 gives the concentration dependence of the parameter K for the systems studied. The extrapolated values of K and the values calculated from Eqn. (18) are given in Table 3; the relationship $(\bar{h}_0^2/M) = bA/M_0$ was used (b is the length of the monomeric unit, M_0 the molecular mass of the monomeric unit, and A the length of the Kuhn segment). The data in Table 3 show that for the first two θ-systems, the experimentally determined values of K_0 are much greater than the theoretical values K_0^{theor}, calculated from Eqn. (18). For polymers in good solvents, these values are similar; in their comparison it must be borne in mind that K_0^{theor} is in fact the limiting value, since for non-ideal solutions it is necessary in Eqn. (18) to take account of the dimensions $\bar{h}^2$ of the coiled molecules in the good solvent.

From the experimental relationships $D(c)$ [88] and $S(c)$ for PS in CH, it is possible to calculate $K^{calc}(c)$ directly from Eqn. (17) (see Fig. 6*a*). Extrapolation gives for PS-1 the value $K_0^{calc} = 1.8\times10^{-19}$ and for PS-2, $K_0^{calc} = 2.0\times10^{-19}$, that is there is a very large difference between the experimental and calculated values of K_0. In addition, the published illustrations[21] can be used to determine the values of K for various PS specimens: the specimen with $\bar{M}_w = 3.16\times10^5$, $\bar{M}_w/\bar{M}_n = 1.02$, and $c = 0.3180$ has $K = 2.0\times10^{-19}$, and the specimen with $\bar{M}_w = 3.52\times10^5$, $\bar{M}_w/\bar{M}_n = 1.53$, and $c = 0.3253$ has $K = 2.3\times10^{-19}$. For PS-2 at $c = 0.3050$, $K = 17\times10^{-19}$, and for PS-1 at $c = 0.3016$, $K = 41\times10^{-19}$.

These examples show that there is a definite relationship between K and the polydispersity and average molecular mass. Comparison of the values of $\bar{D}_0$, calculated from the values of K_0 and K_0^{theor} (see Table 3) shows that the excess broadening (that is the broadening which is not due to the polydispersity) of the boundary of the solutions of specimens of PS in CH and of PVA in BEK is due chiefly not to diffusion but to other factors.

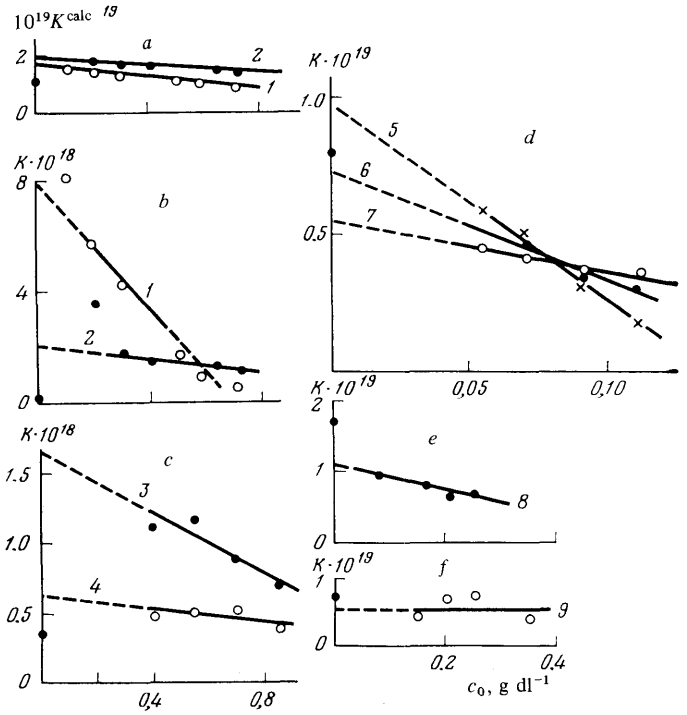


Figure 6. Concentration dependence of the parameter K for the systems: PS–CH, 34° (*a*, *b*); PVA–BEK, 29° (*c*); PPhIA–(DMF–0.25% LiCl), 25° (*d*); PAN–DMF : THF (1 : 1), 25° (*e*); PVC–THF, 25° (*f*). The points on the ordinate correspond to the values of K_0 calculated from Eqn. (18), and the figures give the numbering of the specimens in Tables 2 and 3.

Table 3. Characteristics of the systems studied, related to the determination of the parameter K*.

No.	Polymer	Solvent for the sedimentation; temperature, °C	$10^2\eta_0$, P	M_0	$10^8 b$, cm	$10^8 A$, cm	$\bar{S}_0$, Svedberg units	σ_0, Svedberg units	$K_0\cdot10^{19}$	$10^{19}K_0^{theor}$	$10^6\bar{D}$ (from K_0)	$10^6\bar{D}$ (from K_0^{theor})
1	PS	CH; 34°	0.751	105	2.3	20.0[3]	15.7	3.75	80	1.12	5.1	0.071
2	PS	CH; 34°	0.751	105	2.3	20.0[3]	5.65	1.63	20	1.12	3.5	0.198
3	PVA	BEK; 29°	0.710	86	2.3	17.4[3]	11.7	2.83	16.7	3.64	1.43	0.311
4	PVA	BEK; 29°	0.710	86	2.3	17.4[3]	8.20	1.74	6.40	3.64	0.78	0.444
5	PPhIA	DMF—0.25% LiCl; 25°	0.810	242	12.3	34.0[84]	4.26	0.87	0.97	0.82	0.228	0.193
6	PPhIA	DMF—0.25% LiCl; 25°	0.810	242	12.3	34.0[84]	3.43	0.95	0.73	0.82	0.213	0.239
7	PPhIA	DMF—0.25% LiCl; 25°C	0.810	242	12.3	34.0[84]	2.91	0.89	0.55	0.82	0.189	0.282
8	PAN	DMF—THF (1 : 1); 25°	0.633	53	2.3	21.0[87]	3.64	0.90	1.14	1.72	0.313	0.472
9	PVC	THF; 25°	0.471	62.5	2.3	17.9[85]	5.09	0.98	0.55	0.70	0.108	0.137

* Symbols: M_0 is the molecular mass of the monomeric unit; b the length of the monomeric unit; A the length of the statistical segment; and σ_0 the dispersion of the distribution $g(S_0)$.

The values of $\bar{D}_0$ determined from K_0 and K_0^{theor} for PPhIA in DMF–0.25% LiCl do not differ so markedly, but they show the opposite dependence on the average molecular mass (or on $\bar{S}_0$ from Table 3): the value of D_0 decreases with increase in the average molecular mass of the specimen in the first case, and decreases in the second case, so that the excess broadening of the boundary for this system is not due entirely to diffusion.

An important role is apparently played by the hydrodynamic interactions of the components of the mixture (that is the JOE). The cross-term interactions of the flow of the individual components of a polydisperse polymer should lead to a decrease in the rate of sedimentation for the low-molecular-weight fractions and to an increase in this rate for the high-molecular-weight fractions, and this leads to broadening of the $g^*(S, t)$ curves, similar to diffusion broadening. Extrapolation to $1/t = 0$ apparently takes partial or complete account of this broadening, and leads to an increase in the values of K_0 and $\bar{D}_0$ (see Table 3).

b) The use of model functions to take account of the diffusion broadening of distribution curves with respect to sedimentation coefficients in a single recording

In real systems, the correction for diffusion in the sedimentation of polymers with medium and low polydispersity is comparatively small (10–30%), and the second term in the right-hand side of Eqns. (19) and (20) has the character of a correction, and this makes it possible to take it into account by means of model functions[26,66,89]. This can be done most simply on the basis of the Gaussian function (27) by an iteration method[26,66].

The distribution $g(S)$ in the second term in the right-hand side of Eqn. (19) is replaced by the distribution $g^*(S, t)$, and this in turn is replaced by the function (27), with parameters $S_m = \bar{S}^*$ and $\sigma = \sigma^*$,

$$(\sigma^*)^2 = \int_0^\infty (S^* - \bar{S}^*)^2 g^*(S, t)\, dS \Big/ \int_0^\infty g^*(S, t)\, dS. \qquad (30)$$

The following equations are obtained in place of Eqns. (19) and (22):

$$g(S) = g^*(S, t) \Big/ \left\{1 - \frac{1}{4\tau S}\left[\frac{1}{(\sigma^*)^2} - \frac{1}{S^2} - \left(\frac{S - \bar{S}^*}{(\sigma^*)^2} + \frac{1}{S}\right)^2\right]\right\}, \qquad (31)$$

$$S^* = S + \frac{1}{4\tau}\left[\frac{1}{S^2} + \frac{S - \bar{S}^*}{S(\sigma^*)^2}\right]. \qquad (32)$$

The distribution $g(S)$ obtained can be used again to refine the parameters S_m and σ of the Gaussian curve, after which the calculation from Eqns. (31) or (32) is repeated, etc. It should be noted that this procedure involves not the replacement of the real distribution by a model function[23,90–92] but the determination of the law corresponding to the deformation of this distribution (the denominator in Eqn. (31)).

By proceeding analogously, it is possible to obtain expressions[89] for taking account of the diffusion broadening of the boundary by means of the functions of Schulz[93] and Beasley[94]. Fig. 7*b*, for the specimen PPhIA-5, compares the extrapolation distribution $g(S)$ with the distributions calculated from one sedimentation diagram on the basis of the model functions of Gauss, Schulz, and Beasley[89]. The calculation based on the functions of Gauss and Schulz led to good agreement between the calculated and extrapolation curves $g(S)$, since the models coincide fairly closely with the distribution $g^*(S, t)$ (Fig. 7*a*). At the same time, in spite of the fact that the model based on the Beasley function had nothing in common with the distribution $g^*(S, t)$, the $g(S)$ curve calculated on the basis of this function did not differ greatly from the extrapolation distribution.

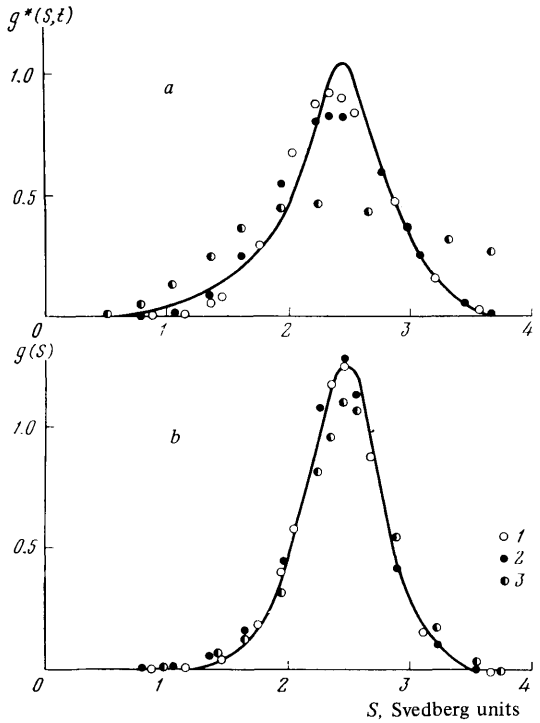


Figure 7. Comparison of the distribution $g^*(S, t)$ for specimen PPhIA-5 ($c = 0.11$ g dl^{-1}) in DMF–0.25% LiCl, $t = 4953$ s (continuous line) with model functions (*a*), and comparison of the extrapolation curve $g(S)$ (continuous line) with the distributions calculated from one recording, based on model functions (*b*): *1*) Gauss; *2*) Schulz; and *3*) Beasley.

Thus when allowance is made for diffusion from a single recording, the slight lack of agreement between the model curve and the real curve $g^*(S, t)$ does not play a significant role, but when the model is completely "separated" from the real distribution $g^*(S, t)$, allowance for diffusion from a single recording leads to distortion of the form of the $g(S)$ curves. Naturally, in real situations, the form of the sedimentation diagrams, the nature of the process by which the polymer is obtained, etc. should influence the type of model function which will make it possible to take account of the diffusion broadening of the distributions $g(S)$.

3. CONCENTRATION DEPENDENCE OF THE SEDIMENTATION COEFFICIENTS OF POLYDISPERSE POLYMERS

For a number of systems (see Table 2), the treatment of the $S(c)$ relationships in the extrapolation of the distributions $G(S)$ to $c = 0$ is carried out in accordance with

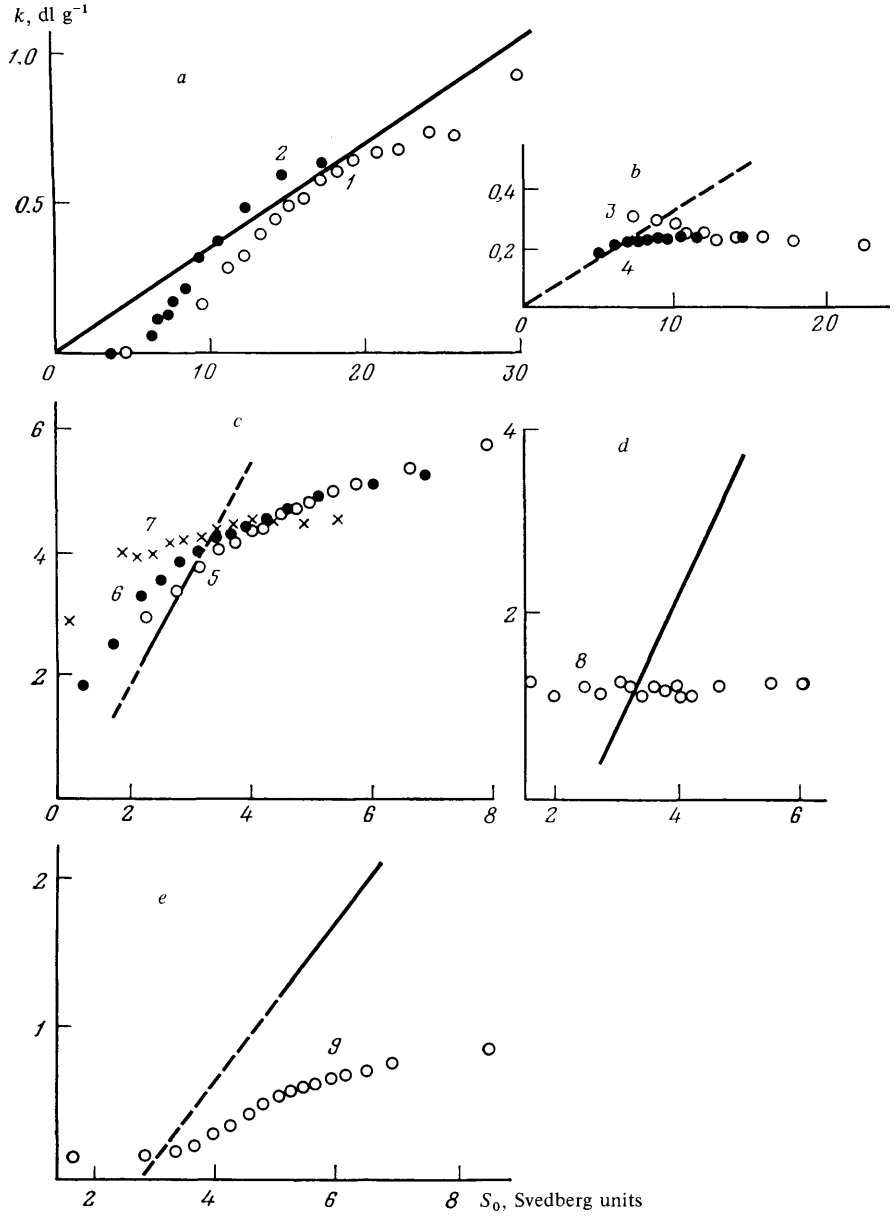


Figure 8. Dependence of k on S_0 for the systems: *a*) PS–CH, 34°; *b*) PVA–BEK, 29°; *c*) PPhIA–(DMF–0.25% LiCl), 25°; *d*) PAN–(DMF : THF = 1 : 1), 25°; *e*) PVC–THF, 25°; the numbers next to the symbols correspond to the numbering of the specimens in Table 2; the continuous and broken lines represent the functions $k(S_0)$ for the fractions.

Eqn. (3). In Fig. 8, the functions $k = k(S_0)$ obtained from these relationships are compared with the same functions for the fractions. The data in Fig. 8 show that polydisperse polymers in good solvents (Figs. 8*c*, 8*d*, and 8*e*) are characterised by a marked weakening of the concentration dependence of the sedimentation coefficients for the high-molecular-weight components, and an intensification of the concentration dependence of the sedimentation coefficients for the low-molecular-weight components. In the system PS–CH (Fig. 8*a*), there is a relatively poor correspondence between the functions for the polydisperse specimens and the fractions.

The following points should be noted regarding the θ-system PVA–BEK (Fig. 8*b*). For this system, a $S(c)$ relationship was not detected[82], but this relationship appeared when a correction was introduced for the pressure μ. The cross-term interactions in the polydisperse polymer compensate one another about the centre of gravity ($\overline{S}$) of the distribution $g(S)$, so that the $\overline{S} = \overline{S}(c)$ relationship (or the analogous functions found from the maxima of the gradient curves) should not be distorted by Johnston–Ogston effects. On the other hand, both theory[50] and experiment[21,54] give a linear dependence of k on S_0 for the case of flexible-chain polymers in a θ-solvent, although

for rigid-chain macromolecules this relationship is apparently more complex[61,62]. In view of these features, the function $k(S_0)$ for the fractions of the system PVA–BEK was estimated from the $\bar{S} = \bar{S}(c)$ relationship for two non-fractionated specimens, and is given by the broken line in Fig. 8*b*. In this system, as in the case of polymers in good solvents, marked differences are observed between the $k(S_0)$ relationships for polydisperse polymers and the analogous functions for homogeneous polymers (fractions).

If it is assumed that diffusion extrapolation does not eliminate completely the broadening of the distributions $g(S)$ due to cross-term interactions, there arises the question of how these interactions influence the concentration dependence of the sedimentation coefficients. The scheme in Fig. 9 can be examined in this connection. The hypothetical distribution with identical relative concentrations of all the components undergoes the usual self-contraction (straight lines *AB* and *CD*) and additional broadening due to cross-term interactions (straight lines *A'B'* and *C'D'*). The concentration dependence $S(c)$ is determined by the difference in the values of S for corresponding points of these straight lines for a given G = const. For the extreme points of the distributions, $A'C' > AC$ and $B'D' < BD$, indicating an increase for low-molecular-weight components, and a decrease for high-molecular-weight components, in the value of the function $\kappa(S_0)$ for polydisperse polymers compared with the same function for the fractions.

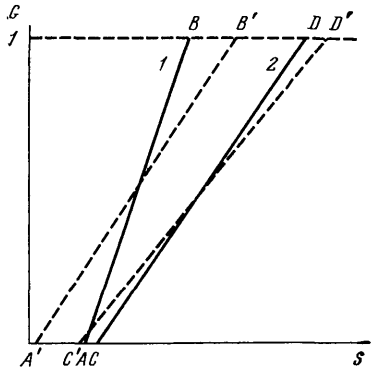


Figure 9. Schematic representation of the influence of effects of the Johnston–Ogston type on the integral distributions $G(S)$; the continuous lines correspond to distributions not perturbed by these effects, and the broken lines represent distributions influenced by these effects. The numbers 1 and 2 correspond to the distributions at concentrations c_1 and c_2 ($c_1 > c_2$).

In the examination of the data in the PS–CH system, it is necessary to take account of the difference by a power of ten between K_0 and K_0^{theor} and K_0^{calc} (see Table 3). It may be assumed that in this system, complete allowance is made for the Johnston–Ogston effects in the extrapolation of $g^*(S, t)$ to $1/t = 0$, so that the functions $k(S_0)$ are similar for the fractions and the polydisperse polymers.

Finally, it should be noted that the interpretation of the concentration dependence of S for polydisperse polymers by means of the scheme in Fig. 9 is inseparable from the concept of local concentration. Thus the concentration dependence of the high-molecular-weight components disappears (the value of k is small), since for these components, the components with higher and lower molecular weights represent a medium with a lower hydrodynamic resistance. Similarly, the accumulation of low-molecular-weight fractions in the sedimentation process may lead to a slight increase in the value of κ.

4. CROSS-TERM HYDRODYNAMIC INTERACTIONS OF THE COMPONENTS IN THE SEDIMENTATION OF POLYDISPERSE POLYMERS

a) Allowance for the JOE of polydisperse polymers

The experimental facts described above leave no doubt that local concentration plays a part in the sedimentation of a polydisperse polymer. Thus in the region of the boundary, the value of the sedimentation coefficient of the ith component will be determined by the concentrations and the interactions of the components with numbers from 1 to i, and in the region of the plateau it will be determined by the concentrations and interactions of all the components. In the general case, it is possible to determine phenomenologically the sedimentation coefficient of the ith component in a solution of q components of a polydisperse polymer as follows[8,95]:

$$S_i = S_{0i} \Big/ \left(1 + k_i c_i + \sum_{j=1}^{q} k_{ij} c_j\right); \; j \neq i; \; i = 1, 2, \ldots, q, \qquad (33)$$

where S_{0i} is the sedimentation constant of the ith component, and the coefficients k_i and k_{ij} were defined earlier. Eqn. (33) represents a generalisation of Eqns. (3) and (12), and is applicable for sufficiently dilute solutions, since in the denominator of the right-hand side the terms with the products (squares) of the concentrations have been discarded. If the concentrations c_i are taken as the concentrations in the region of the plateau, Eqn. (33) gives the values of the sedimentation coefficients in the region of the plateau.

As already noted, for an ideal solvent, $k_{ij} = k_j$, and the following equation is obtained in place of Eqn. (33):

$$S_i = S_{0i} \Big/ \left(1 + \sum_{j=1}^{q} k_j c_j\right), \qquad (34)$$

and for the intermediate region (see Fig. 10):

$$S_i = S_{0i} \Big/ \left(1 + \sum_{j=1}^{i} k_j c_j^*\right). \qquad (35)$$

A slightly different argument may be used. It may be assumed that the solvent for the ith component is the solution of the components from 1 to $i - 1$ (Fig. 10), and the influence of these components on the sedimentation of the ith component reduces to a decrease in the rate of its movement as a result of the viscosity of the medium. Neglecting quadratic terms, the following relationships are obtained for the viscosity η of the solution of the $i - 1$ components:

$$\frac{\eta - \eta_0}{\eta_0 c} \simeq [\eta]; \; c = \sum_{j=1}^{i-1} c_j^*; \; [\eta] = \sum_{j=1}^{i-1} [\eta]_j,$$

where $[\eta]_j$ is the characteristic viscosity of the jth component. The obvious relationship $S_1\eta_1 = S_2\eta_2$ (the indices 1

and 2 here correspond to different solvents) and Eqn. (3) give:

$$S_i = S_{0i}\Big/\left[1+\left(\sum_{j=1}^{i-1} c_j^*\right)\left(\sum_{n=1}^{i-1}[\eta]_n\right)\right](1+k_ic_i^*).$$

Rejection of the "cross-terms" $c_j[\eta]_n$, $j \neq n$, gives:

$$S_i = S_{0i}\Big/\left(1+\sum_{j=1}^{i-1} c_j^*[\eta]_j\right)(1+k_ic_i^*). \quad (36)$$

For flexible-chain polymers, $k_j = A[\eta]_j$, where A is a constant for a given polymer–solvent system[3, 61, 62]. Using this relationship, Eqn. (36) can be transformed to

$$S_i = S_{0i}\Big/\left(1+\sum_{j=1}^{i-1} k_jc_j^*/A\right)(1+k_ic_i^*).$$

In the particular case where $A = 1$, Eqn. (36a) becomes Eqn. (35).

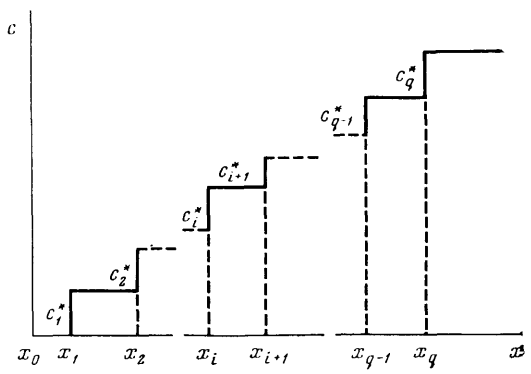


Figure 10. Schematic representation of the dependence of the concentration c on the coordinate x in the centrifuge cell in the sedimentation of a polydisperse polymer consisting of q components.

In the calculation of the true concentrations of the components c_i^0, the idea of additivity of the paired interactions is used, that is it is assumed that for an arbitrary pair of components i and j, by analogy with Eqns. (13), (15a), and (15b), the following relationships are applicable:

$$\psi_{ij} = S_{0i}/S_{0j},\ i = 1, 2, \ldots q; \quad (37)$$

$$c_{ij}^0 = c_i^*(y_j - y_i)/[y_j^{1-\psi_{ij}} - 1],\ i < j; \quad (38a)$$

$$c_{ji}^0 = c_i^*y_i + c_j^*y_j - c_{ij}^0, \quad (38b)$$

where c_{ij}^0 is the concentration of the ith component in the original mixture, calculated from c_i^* with allowance for the interaction with the jth component, neglecting the influence of the other components of the mixture. The sedimentation constants S_{0i} are determined from Eqns. (34), (35), and (36a). Averaging with respect to the interactions with all the components gives finally:

$$c_{i0} = \sum_{j=1}^{q} c_{ij}/(q-1),\ j \neq i. \quad (39)$$

The change to the distribution $g_i(S_{0i})$ is brought about by means of the relationship:

$$g_i(S_{0i}) = c_{i0}x_i/[1 + m(r_i - 1)]. \quad (40)$$

For centrifuges fitted with the usual refractometric optics, the experiment gives the distributions of the displacements $z_i(x_i)$. Since the calculations require the values of the concentrations throughout, it is necessary either to carry out a separate diffusion experiment or to make use of the relationship[48, 65]:

$$R\Delta x\sum_{i=1}^{q} z_iy_i = c_0, \quad (41)$$

where R is the refractometric coefficient, and $\Delta x = x_i - x_{i-1}$. By determining $R\Delta x$, it is possible to find c_i^*:

$$c_i^* = z_iR\Delta x\,. \quad (42)$$

In addition, it is necessary to know the function $k_i = k_i(S_{0i})$, preferably determined in experiments with narrow fractions. In the case of the linear relationship

$$k_i = \pm a + bS_{0i} \quad (43)$$

Eqn. (35) gives:

$$S_{0i} = S_i^*\left(1+\sum_{j=1}^{i-1} k_jc_j^* \pm ac_i^*\right)\Big/(1 - S_i^*bc_i^*). \quad (44)$$

The system of equations (43) and (44) is solved successively, beginning from $i = 1$.

Thus the theory takes account of the following factors influencing the form of the sedimentation curves: the hydrostatic pressure, the concentration dependence of the sedimentation coefficients, the sector form of the cell, and the hydrodynamic interaction of the components (JOE). Only the part played by diffusion is not taken into account. The last section will deal with the characteristic features of the application of this theory to specific systems, and in particular, methods of eliminating the diffusion broadening of the distributions $g(S)$.

b) Determination of the distributions $g(S_0)$

Allowance for the JOE not only gives a new series of equations for calculating $g_i(S_{i0})$ but also makes it possible to take a fresh look at various problems of sedimentation analysis[96]. The disappearance of the high-molecular-weight "tails" of the MMD of a number of PS and PE specimens during sedimentation was first detected by Belyaev[97]. It is obviously incorrect to attribute this fact to dilution or to a decrease in concentration in the region of the plateau[98, 99]. The concept of the JOE provides a comparatively simple explanation of this phenomenon. As a result of cross-term interactions in the sedimentation process, there is an accumulation of the low-molecular-weight components and a relative decrease in the concentration of the high-molecular-weight components. With the passage of time, this leads to a displacement of the maximum towards smaller values of S and to disappearance of the "tail" of the distribution.

In the determination of the MMD of highly polydisperse polymers by the coordinate method[37], an increase in the height of the maximum on the $g(S, t)$ curves of polyethylene (PE) in α-bromonaphthalene at 110°C with increase in the distance between the fixed coordinate and the line corresponding to the start of sedimentation was detected. The displacements (and concentrations) for different fixed coordinates in fact correspond to different stages of the sedimentation process. The farther the coordinate from

the line corresponding to the start of sedimentation, the stronger the manifestation of the cross-term interactions (see Eqn. (38a)) and the higher the maxima on the $g(S, t)$ curves for PE, corresponding to fairly low-molecular-weight components. These results show that the JOE is marked in the sedimentation of strongly polydisperse polymers, and it is for this reason that it is hardly possible to determine correctly the concentration of low-molecular-weight compounds in a polymer without allowance for this effect[41].

Table 4. Characteristics of the distribution $g(S_0)$, calculated from one recording by different methods.

c, g dl^{-1}	$10^{-3}t$, s	Allowance for the JOE		Method (Refs. 26, 66)	
		$\bar{S}_0$, Svedberg units	σ_0 Svedberg units	$\bar{S}_0$, Svedberg units	σ_0 Svedberg units
		PS-1 in CH (34°)			
0.7110	3.02	14.1	4.48	15.1	3.93
	3.62	14.4	4.12	15.3	3.46
	4.22	14.6	4.20	15.5	3.29
	5.12	14.7	4.11	15.4	3.18
0.3016	0.887	19.0	7.39	18.7	5.60
	1.487	18.5	6.73	17.3	4.17
	2.387	18.2	6.16	17.7	4.65
	3.287	17.7	5.85	17.2	4.23
0.1142	1.22	16.2	6.41	14.7	4.62
	1.82	17.1	6.59	16.0	5.35
	2.42	16.7	5.95	15.6	4.77
average value*		17.4±0.8	6.3±0.3	16.4±1.0	4.6±0.3
		PPhIA-5 in DMF–25% LiCl (25°C)			
0.110	1.92**				
	3.12	2.88	0.838	calculations impossible	
	4.32	3.04	0.875		
	6.24	3.10	0.895		
	7.32	3.03	0.924		
0.090	1.304				
	2.493	2.94	1.051		
	3.693	2.96	1.065	3.78	1.151
	4.893	3.13	1.059	3.94	0.951
	6.093	3.62	1.261	4.07	1.012
0.070	0.974				
	2.17	3.26	1.201	3.46	1.170
	3.37	3.27	1.179	3.45	1.033
	5.17	3.35	1.121	3.53	0.827
	6.37	3.44	1.155	3.56	0.794
0.055	1.056				
	1.953	3.26	1.201	3.46	1.170
	2.853	3.27	1.179	3.45	1.033
	4.053	3.35	1.121	3.53	0.827
	4.953	3.44	1.155	3.56	0.794
average value		3.30±0.18	1.13±0.08	3.70±0.18	0.97±0.14

* For PS-1, the values for $c = 0.711$ and the values for the first recording $c = 0.3016$ were not included in the averaging (for explanation see text); for PPhIA-5, the values for $c = 0.11$ and the values for the second recording ($t = 2.493 \times 10^3$ s) $c = 0.09$ g dl^{-1} were not included.
** The first recordings for all concentrations of PPhIA served only for the determination of the end of the $g(S)$ curve (see text).

Table 4 gives the characteristics of the distributions $g(S_0)$ for specimens of PS-1 in CH at 34°C and of PPhIA-5 in a DMF–0.25% LiCl mixture at 25°C, calculated from a single recording using the theory taking account of the JOE or by a method[26,66] based on the mathematical formalisation of the extrapolation procedures, that is on the empirical values of the diffusion parameter K and the empirical functions (43).[76] In the calculations by the first method, the distributions $g_i^*(S_i)$ are first corrected with allowance for the concentration dependence of the sedimentation coefficients, pressure, the JOE, and dilution, after which (for $c = 0$) a correction is introduced for diffusion from the theoretical value of the parameter K.[76] For polystyrene, the correction for the $S(c)$ dependence was introduced from Eqn. (43) ($a = 0$, $b = 0.036$ dl g^{-1}) for both methods. The algorithms for the calculations were naturally different in these cases, since the original concepts are diametrically opposed (local concentration and plateau concentration). The sedimentation coefficients of PPhIA were corrected for the concentration dependence using different relationships: the first method (with allowance for the JOE) was based on data for fractions: $k_i = 0$ for $S_i \leq 0.75$; $k_i = -1.11 + 1.48\, S_{i0}$ for $S_i > 0.75$ (Svedberg unit); the second method was based on data for non-fractionated specimens $k_i = 2.12\sqrt{S_{0i}}$.

As already noted, the cross-term interactions of the components of a specimen non-uniform with respect to mass lead to the loss of the distribution "tail". Theory[95] provides a somewhat unusual method for reconstructing the end of the $g_i(S_{i0})$ curve. It is assumed that the true end of the distribution is the point obtained for short ultracentrifuging times. To supplement q graphical fractions (with concentrations $c_i^* > 0$), n "correction" components (with concentrations $c_j^* = 0$, $j > q$) are introduced into the computer store. Here it should be noted that the calculations are carried out by computer, and the complexity of the mathematical treatment is no obstacle to the determination of $g_i(S_{i0})$. The calculations using Eqns. (37)–(39) give non-zero concentrations for the "corrected" components.

Fig. 11 gives the distributions $g(S_0)$ for PS-1 in CH, $c = 0.3016$ g dl^{-1}, calculated by the first method with allowance for the JOE (circles). One of the curves was calculated with restoration of the "tail" for the values $q = 26$ and $n = 6$ (empty circles) and differs little from the curve obtained without restoration of the "tail" (filled circles). The calculation by the second method[26,66] gives a distribution which is very much sharper (crosses), and which differs considerably from the distribution determined by the first method. It is possible to point to three reasons for this sharpening. Firstly, the loss of the "tail" in the calculation by the second method[26,66] is irreversible. Secondly, the diffusion contribution to the broadening of the boundary is greatly over-estimated as a consequence of the JOE.[76] Thirdly, when there is appreciable diffusion, there is significant distortion of the $g(S_0)$ curves as a consequence of the difference between the model (Gaussian function) and the real distribution $g^*(S, t)$, whereas when there is little diffusion, these differences are not significant[89].

The generally accepted extrapolation procedures[2-4] lead to the following characteristics of the $g(S_0)$ distributions for the specimens studied: for PS-1, $\bar{S}_0 = 15.7$ and $\sigma_0 = 3.80$ Svedberg unit; for PPhIA-5, $\bar{S}_0 = 3.6$ and $\sigma_0 = 0.98$ Svedberg unit. Comparison of these parameters with the data in Table 4 confirms the familiar fact that extrapolation of the $g(S)$ curves in the case of polymers (PS) of medium polydispersity leads to a loss of the fine details of the distributions (for example, poorly resolved maxima) and the "tail", and to sharpening of the distributions (compare the values of σ_0).

The data obtained by different methods for the polymer PPhIA-5 with a low polydispersity show better agreement with one another (Table 4), but it was not possible, by the second method, to determine $g(S_0)$ for all recordings at $c = 0.11$ g dl^{-1} and for the first recording at $c = 0.09$ g dl^{-1}, whereas the calculations using the theory of Ref. 95 can be carried out for all values of c and t.

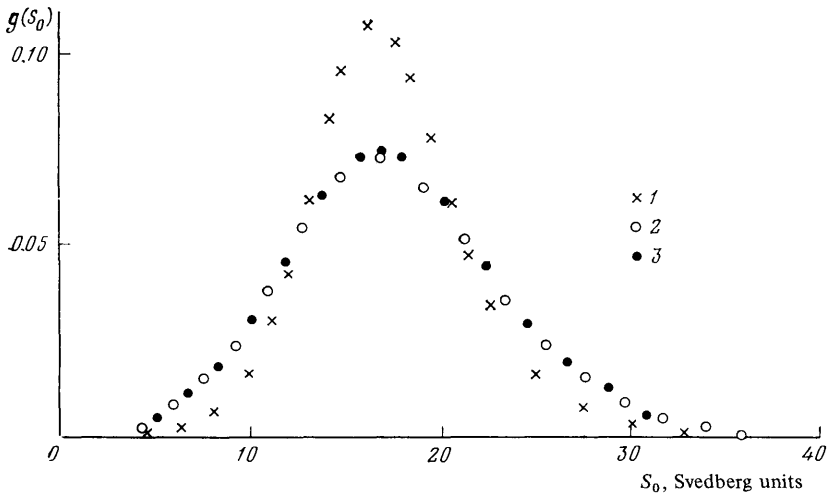


Figure 11. Distributions $g(S_0)$ for PS-1 in CH, 34°, $c = 0.3016$ g dl^{-1}, calculated from one recording for $t = 3287$ s by the published method[26,66] (*1*) and from theory, with allowance for the JOE, with (*2*) and without (*3*) additional components.

The slight decrease in the value of $\bar{S}_0$ in the calculations by the first method is apparently due to two features. Firstly, the theory[95], strictly speaking, refers to ideal systems. The results of the study of the JOE of binary mixtures in a good solvent indicate that the theory of Ref. 29 in this case is confirmed quantitatively only in the limit as $c \to 0$.[71] For PPhIA-5, the calculation algorithm should be based not on Eqn. (35) but on Eqn. (36). Secondly, the first recording was carried out too late, and part of the "tail" was lost. This applies particularly to the data for $c = 0.11$ g dl^{-1}.

A characteristic feature is that the parameters of the distributions $g(S_0)$ calculated by the first method have a much smaller scatter than the analogous values calculated by the second method. All the results obtained using Eqns. (35)–(44) must be regarded as preliminary—they can be improved considerably—whereas it is practically impossible to improve the calculation by the procedure of Refs. 26 and 66. The last approach preserves some of the unsatisfactory features characteristic as a whole of the extrapolation of the distributions, which is based on a number of arbitrary assumptions: simple additivity of the factors operating and the movement of the components, neglect of the cross-term interactions of the components, and the concept of plateau concentration. The approach based on allowance for the JOE and the concept of local concentration appears more correct[95,96].

V. CONCLUSION

Detailed analysis of the experimental data leaves no doubt that the cross-term hydrodynamic interactions of the components—the Johnston—Ogston effect (JOE)—play an important part in the sedimentation of polymers of high and medium polydispersity, and can be observed in the sedimentation of polymers of low polydispersity. Such phenomena as the displacement of the maxima, the loss of the "tail", the increase in the height of the maximum of the distribution $g^*(S, t)$ with increase in the distance between the fixed coordinate and the line corresponding to the start of the sedimentation, the non-diffusion broadening of the $g(S)$ curves, the decrease in the effect of the $S(c)$ dependence for the high-molecular-weight components of a mixture, and the increase in its effect for the low-molecular-weight components, can be explained only on the basis of the JOE and the concept of local concentration.

The distinctive feature of the situation is that no method has been found for making rigorous allowance—via the equations of motion—for the cross-term interactions of the components undergoing sedimentation, even for a binary mixture; the expectation of an exact theory of the sedimentation of many-component systems is therefore illusory. Thus at present the only possible approach is that based on the principle of additivity of the paired interactions[95].

The fact that the problem of the sedimentation of polydisperse polymers is insoluble theoretically, and decades of the preferred application of the extrapolation method, the concept of plateau concentration, unjustified single-recording and single-concentration approximations, and the view that different effects are "compensated" on the one hand have not stimulated serious experimental-methodological studies and on the other have effectively "immunised" research workers against theoretical work. This is the only possible explanation for the fact that very important work[48,75] has remained neglected, although the first of the works cited provides a theoretical basis for the treatment of sedimentation measurements on fractions, and the second makes it possible to carry out a quantitative estimation and allowance for the role of the diffusion factor in the sedimentation of polydisperse polymers[26,66,76,86,89].

The natural failure of the concept of plateau concentration and the development, on a new basis, of the concept of local concentration[95] indicates not only the usefulness but also the necessity of determining $g(S_0)$ from a single concentration, since for polymers of medium polydispersity, the extrapolation of the $g(S)$ distributions to $c = 0$ has no physical foundation. Using Fujita's theory[75], it is possible from a single recording to take account of the diffusion broadening of the $g^*(S, t)$ curves[26,66,89]; thus the required $g(S_0)$ distribution is obtained by computer

calculation from a single sedimentation diagram. Preliminary data[96] indicate that this method of determining $g(S_0)$ is promising.

In conclusion, the calculation procedure should be mentioned: it is not simple, and can only be carried out by computer. Eqns. (8) and (16) are first used to find the distribution $g^*(S, t)$ for which it is possible to introduce a correction for diffusion broadening (see Part III); the choice of the values of K is discussed below.

As already noted, for polymers of high and medium polydispersity, the required distribution $g(S_0)$ (or $g(M)$) is distorted by the loss of the "tail". The first recording must therefore be fixed at different times of ultracentrifuging. The time of ultracentrifuging should not be so short that the introduction of a correction for dispersal by the formal rule has no influence on the values of the sedimentation coefficients.

Using the parameter of the distribution $g(S)$, the diffusion problem is solved for the end of the distribution of the displacements, obtained in the first recording. In this case it is not strictly necessary to determine the entire distribution; it is sufficient to determine only the position of the end of the curve. The overall result gives the value of the sedimentation coefficient for the end of the distribution S_{end}, from which the number of components "lost" is subsequently determined.

Eqns. (41) and (42) are used to calculate c_i^*; the values of the sedimentation constants of the components S'_{i0} are then found in a first approximation from Eqns. (43) and (44), and this makes it possible to take account of the JOE from Eqns. (37), (38a), (38b), and (39). The corrected concentrations of the components c_{i0} can then be used to obtain more accurate values of the sedimentation constants S_{i0} and the functions $g_i(S_{i0}, t)$ from Eqn. (4). Since the concentration effects are eliminated, the diffusion broadening can be taken into account from the theoretical value of the parameter K (see Eqn. (18)). Alternatively, the values of K obtained from diffusion experiments can be used.

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Identification of Substances in Gas Chromatography

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Methods for the qualitative analysis of substances separated chromatographically have been examined. Particular attention has been paid to methods which have been intensively developed in recent years for identifying substances from their chromatographic characteristics without the use of a standard. The bibliography contains 265 references.

CONTENTS

I. Introduction 714
II. Methods of identification using standards 714
III. Methods of identification without the use of standards 716

I. INTRODUCTION

One of the central problems with which research workers have been concerned throughout all stages of the development of the gas chromatographic method is the identification of substances separated chromatographically. In almost all monographs on gas chromatography, chapters have been devoted to qualitative analysis, and this question has also been dealt with in a number of review articles. In most of the latter, attention has been concentrated chiefly on one aspect of the problem. Monographs and reviews on this subject do not deal with recent work. In the most detailed review devoted to the contribution of gas chromatography to identification [1], published material up to only 1969 was reviewed. The most significant progress in this field, however, which has made it possible to reach conclusions regarding the structure of a substance from its gas chromatographic behaviour and to predict the chromatographic behaviour of a substance from its structure and physicochemical properties, has been made in recent years.

The present review deals with data on qualitative gas chromatographic analysis published up to and including 1974. Since zone identification based on additional operations with the components of mixtures before and after gas chromatographic separation has been dealt with in sufficient detail in reviews and monographs, for example in Ref. 2, the present review was restricted to an examination of methods which use only gas chromatographic data for identification. In addition to a discussion of methods of identification using standards, particular attention has been paid to the latest achievements in the development of correlation methods and methods based on predictive retention calculations, not involving the use of standards.

II. METHODS OF IDENTIFICATION USING STANDARDS

In these methods, the qualitative analysis of a mixture is carried out by comparing the chromatogram of the specimen being studied with the chromatograms of standard substances or with tabulated data. The identity criterion is the coincidence of the retention data of the substance being analysed and the standard, since under identical and correctly chosen experimental conditions, the retention values should be physicochemical constants of the substances, characterising their distribution in the gas–sorbent system [3-5].

In the first version, which is very frequently used in practice, the identification is carried out by comparing the retention values, measured under identical conditions, of the components of the mixture being analysed and standard substances, the presence of which in the material being studied is assumed. It is concluded that a substance is present in a mixture when the retention times coincide (for the analysis of standard directly before or after the chromatographic study of the specimen) or from the increase in the corresponding peak on the chromatogram (in the case where the assumed standard substance is added to the mixture being studied) [3]. The probability of correct identification depends on the number of substances eluted close to one another and on the accuracy of the measurement of the retention volume, and was characterised quantitatively by Klein and Tyler [4] by the magnitude of the "peak density" (the ratio of the total number of peaks to the total number of possible separations in a given interval). The reliability of the identification is increased if the chromatographic separation is carried out on two stationary phases of different polarity [3-5], since components having identical solubilities in one stationary phase in most cases have different solubilities in another. According to Brown [6] it is best to use a combination of non-polar, electron-donor, and electron-acceptor phases. Super-selective sorbents are effective for this purpose.

If the analysis is carried out in parallel on several columns operating under identical conditions, it is possible to obtain the so-called chromatographic spectra of substances. This method was first proposed by Klouwen and Ter Heide [7], who showed for the case of aliphatic compounds and monocyclic and bicyclic terpenes that each class of substance is characterised by a strictly definite form of the curves representing the retention on five stationary phases. Chromatographic spectra have been used for the qualitative analysis of organic substances by a number of workers [8-11]. Franc and Michajlova [8,9] showed that if the same specimen volatiliser and the same detector are used, the chromatographic spectra, like optical spectra, are specific for each individual substance. The possibilities for the identification of the components of mixtures are extended considerably by switching four columns with different stationary phases in pairs in the same apparatus; in this way, eight different versions of the analysis are carried out [11].

The method of standards is widely used in laboratories, but it requires on a priori knowledge of the possible composition of the mixture being analysed and the availability of standard substances for comparison.

In the second version, the components of a mixture are identified by comparing their retention data with data previously obtained by other workers and summarised in tables. Primary gas chromatographic data—retention

times t_R or retention volumes V_R—cannot be used, since they depend on the conditions of their determination. To eliminate this influence, either absolute or relative retention values are used.

Absolute retention characteristics—the specific retention volumes V_g and the distribution coefficients K [12-14] (reference tables [15-19])—are sufficiently reliable criteria for identification if they are accurately determined [20]. This last feature is responsible for the fact that these characteristics are not very widely used, since the accurate reproduction of the conditions of analysis, particularly the quantity of stationary phase in the column, is an extremely tedious task. For the identification of substances, it is preferable to use relative retention characteristics [3]. When the analysis is carried out at the appropriate temperature using the column and standard substance given in the literature, the retention times or volumes related to the corresponding values for the standard are free from the influence of the other conditions of the experiment and can be used to identify the components of the mixture being separated. The relative retention characteristics are given in general form by the equation [21]

$$R^{rel} = p\left(k + \frac{R_x - R_1}{R_2 - R_1}\right), \quad (1)$$

where R_X, R_1, and R_2 are the reduced retention values for the substance being studied and two standard substances respectively; and p and k are constants characteristic of the chosen system of coordinates. In the simplest case when $p = 1$, and $k = R_1 = 0$, the relative retention volume V_R^{rel} (or retention time t_R^{rel}) are obtained.

The relative retention volumes of representatives of the principal classes of organic substance have been tabulated [15-18,22-29]. Of particular interest are the tables of Schupp and Lewis [16], in which retention data are collected for 209 stationary phases and 26 carriers at different temperatures. An edition of tables of retention values has been planned in the USSR Committee of Standards.

An unsatisfactory feature of the method is that a large number of varied compounds are used as standard substances. In spite of an IUPAC recommendation [30], in which it was proposed that the choice of standards be restricted to several substances readily available in pure form (n-butane, 2,2,4-trimethylpentane, benzene, *p*-xylene, naphthalene, butan-2-one, cyclohexanol, and cyclohexanone), different research workers continue to determine V_R relative to any substance which they regard as convenient.

In 1960, Smith [31] proposed that a single substance—"theoretical nonane"—be used as standard. The retention values of "theoretical nonane" are obtained from an analysis of a mixture of n-hydrocarbons by extrapolating the linear relationship between the logarithms of the retention times and the number of carbon atoms in the molecules. To determine the retention relative to "theoretical nonane" R_{X9}, any alkane is added to the mixture being studied, and the retention volume relative to it is calculated. The above linear relationship is then used to determine the retention volume of the hydrocarbon used relative to n-nonane, and the two quantities obtained are multiplied. If the use of an n-alkane is difficult for any reason (analysis on columns containing polar sorbents), the use of the retention value relative to "theoretical n-pentanol", defined analogously, is proposed [31].

The "theoretical nonane" system was further developed by Smith and Evans [32-36]. For high column temperatures, an analytical method was proposed instead of graphical extrapolation [35]. Other retention values can also be recalculated to R_{X9} units, so long as V_R for four n-hydrocarbons are known [34]. The possibility of using a system of secondary standards [36] and of predicting retention values for compounds from the molecular formulas has also been examined [37-39]. The accuracy of the determination of the R_{X9} values, however, depends on how far the primary standard is separated from n-nonane.

A more general solution of the problem of the choice of standards was proposed by Kovats', who recommended the determination of relative retention data using the homologous series of n-alkanes as standards [40,41]. The choice of this series is most natural, since the n-alkanes represent as it were a "zero structure", on the basis of which it is possible to reproduce the structure of all organic substances. Kovats called the new parameter the "retention index". The data are expressed on a logarithmic scale; the retention indices are determined from Eqn.(1) for $p = 100$, $k = n$, $R_1 = \lg R_n$, $R_2 = \lg R_{n+1}$, $R_X = \lg R_X$ (n and $n + 1$ are the numbers of carbon atoms of the n-alkanes diluted immediately before and after the substance being determined). Since for n-alkanes, $\lg R$ is a linear function of the number of carbon atoms in the molecule, the denominator in Eqn.(1) is replaced by b—the slope of the straight line obtained by plotting $\lg R$ against n (b is determined for n-alkanes having $n \geq 6$).

Kovats' system of retention indices is now generally accepted. According to the Recommendation of The Data Sub-Committee For The Publication Of Retention Data [42], and the well-founded opinion of a number of research workers [20,43-53], it provides the most convenient and promising method of characterising retention in gas chromatography. When the retention times are measured accurately, and the temperature of the column is maintained to within 0.1°, [54,55] the retention indices have a high reproducibility, which reaches $\pm(0.03-0.05)$ units [52,56]; the reproducibility of the indices in different laboratories often lies in a range of ± 1 unit [51,52]. A detailed review [57] has been devoted to the problem of applying Kovats' indices in gas chromatography.

In addition to its indisputable advantages, Kovats' system of indices also has some unsatisfactory features. These include the comparatively tedious calculations and the fact that the n-alkanes are not always the most convenient reference substances. Thus in analysis on polar stationary phases, the characterisation of low-boiling polar substances requires the use of high-boiling n-alkanes, because of the weak retention of the latter on polar phases. The simultaneous analysis of high- and low-boiling substances under identical conditions is inaccurate.

The subsequent improvement of Kovats' system of indices has taken place in two directions: 1) simplifcation and an increase in the speed of the calculations, and 2) the use of other series of standard substances instead of n-alkanes and the development of systems similar to Kovats' system. Graphical methods have been proposed in order to increase the speed of calculations [58-60]. The accuracy of the values obtained is low, however. In place of Kovats' logarithmic index, an arithmetic index (also linear) was introduced ($p = 100$, $k = n$, $R_1 = R_n$, $R_2 = R_{n+1}$). [61-65] The problem of calculations is now being solved by the use of computers and special programs for calculating retention indices [66-69].

To avoid the difficulties in the identification of polar and high-boiling substances in Kovats' system, some workers propose that the use of n-alkanes as standards be

replaced by the use of other homologous series: androstane and cholestane for the characterisation of the gas chromatographic retention of steroids (the "steroid number" of Vanden Heuvel and Horning)[70,71]; linear polyphenyls for polyphenyl compounds (the "phenyl number" of Habgood and Harris)[72]; polyacenes for condensed aromatic and heterocyclic systems[73]; dimethylsiloxanes for methylpolysiloxanes ("dimethylsiloxane number")[74-76]; n-alcohols[77]; n-propyl esters[78]; and methyl n-alkyl ketones[79]. For the analysis of lipids, the methyl esters of saturated[80-82] or monounsaturated[83,84] normal acids have been recommended as standards ("equivalent chain length system"). Thus there is a danger of an increase in the number of proposed series of standards, and the problem of standardising retention data may arise again.

The above systems of standards are mainly applicable only for the characterisation of definite groups of substances, and often show poor agreement with one another[85]. For the recalculation of data to Kovats' system, if the indices of the standards I_1 and I_2 are known, the following equation can be used[86]:

$$I = (I_2 - I_1)\frac{\lg R_x - \lg R_1}{\lg R_2 - \lg R_1} + I_1. \qquad (2)$$

The logical conclusion of improvements to the system of retention indices is the introduction of a generalised retention index I_a,[87] which provides for the use, as fixed points, of any homologous series of substances with functional group X_a. The change from one scale of standards to another is brought about using the equation

$$I_a = I_b - I_b(a) + 100\,n(a), \qquad (3)$$

where I_a and I_b are the retention indices of the substances on the scales of the standards a and b respectively; and $I_b(a)$ is the retention index of the substance a with number of carbon atoms $n(a)$ on the scale of standards b.

Systems of expressing gas chromatographic data with an altered scale, such as the "carbon numbers"[80,81], the "methylene unit"[88,89], and the "standardised retention energies"[90,91] must be regarded merely as particular cases of Kovats' system; their adequacy has been demonstrated[92].

There are at present several systematic reference tables of retention indices[19,40,93]. The reference tables of McReynolds[19] are particularly extensive, and give the retention indices of substances on 26 stationary phases for rigorously standardised conditions. In addition to the quantities mentioned, Walraven and Berezkin[21] proposed another two quantities—the relative index ($p = 1$, $k = 100\,n$, $R_1 = 0$, $R_2 = R_n$) and the retention exponent ($p = 100$, $k = 1$, $R_1 = R_A$, $R_2 = R_B$).

The relative retention values are characterised by approximately equal accuracy (equivalent quadratic deviations 0.50–0.75%). For systems with two standards, the increase in the error resulting from the error of the measurement of the retention of the second standard is compensated by the significant of the correlation coefficients. The retention indices give more accurate results than the relative retention volumes only when the substance being analysed and both n-alkanes are introduced simultaneously on to the column[21]. The retention times of the n-alkanes should be measured as accurately as possible, since it has been shown from Erdey's equation[94,95] that these measurements introduce the greatest errors into the value of the retention index.

What has been said above applies chiefly to the accuracy of determinations in a given laboratory. The accuracy and the reproducibility of relative retention values in different laboratories are much lower. One of the chief reasons for the poor reproducibility of retention data between laboratories is the adsorption of substances at gas–liquid and liquid–solid carrier interfaces. The adsorption properties of these interfaces depend on the conditions of preparation of the sorbent[96,97].

To obtain constants which are independent of the conditions of the experiment and the method of preparing the sorbent, it is necessary to take account of the adsorption on the surfaces between the phases and to determine the relative retention values using the equations proposed by Berezkin and coworkers[98]:

$$\frac{V_N}{V_{N_{st}}} = \frac{K_L}{K_{L_{st}}} + \lambda\frac{1}{v_{L_S}};$$

$$\lambda_1 = \frac{(K_{GL}K_{L_{st}} - K_{GL}\cdot K_L)S_{L_S} + (K_S - K_{S_{st}})K_L K_{L_{st}} S_{S_S}}{K^2_{L_{st}}}, \qquad (4)$$

where V_N and $V_{N_{st}}$ are the pure retention volumes of the substance and the standard respectively; K_L and $K_{L_{st}}$ the distribution coefficients of the substance and the standard between the gaseous phase and the stationary liquid phase; K_{GL} and $K_{GL_{st}}$ the distribution coefficients of the substance and the standard in the system formed by the gas and the surface of the stationary liquid phase; K_S and $K_{S_{st}}$ the distribution coefficients of the substance and the standard in the stationary liquid phase–solid carrier system; v_{L_S} the volume of the stationary liquid phase corresponding to 1 g of carrier; S_{L_S} the area of the surface of separation between the gas and the stationary liquid phase, corresponding to 1 g of carrier; and S_{S_S} the specific surface of the solid carrier. If the substance chosen as standard is one for which the retention in the column is determined chiefly by solution, $K_{GL_{st}} = K_{S_{st}} = 0$ and Eqn.(4) is simplified.

The following equation has been proposed for the retention indices[98]:

$$I = 100n + 100\frac{\lg K_L - \lg K_{L_n}}{\lg K_{L_{n+1}} - \lg K_{L_n}} + \frac{43\lambda_2}{\lg K_{L_{n+1}} - \lg K_{L_n}}\cdot\frac{1}{v_{L_S}}, \qquad (5)$$

where $\lambda_2 = \lambda_1 K_{L_n}/K_L$; and K_{L_n} and $K_{L_{n+1}}$ are the distribution coefficients of the n-alkanes with n and $n+1$ carbon atoms between the gaseous and liquid phases. An analogous equation was proposed for the case where capillary columns are used[99].

Allowance for adsorption factors is necessary to obtain reliable results in qualitative analysis using tabulated retention values. This is particularly important in cases where the polarities of the substances being analysed and the stationary phases differ considerably.

III. METHODS OF IDENTIFICATION WITHOUT THE USE OF STANDARDS

From the initial development of gas chromatography, the inconvenience and disadvantage of the use of standard substances have directed research workers to the search for other methods of identification. Considerable progress in this field has been achieved by studying the relationship of the molecular characteristics and structures of substances to their gas chromatographic behaviour, with generalisation and transfer of the observed relationships to other series of compounds. The methods to be examined do not involve the use of standards in the

sense that they do not require the availability of the assumed components of the unknown mixture or the corresponding tabulated data.

The chief methods of identification without the use of standards are as follows: 1) the use of linear correlations between the physicochemical characteristics of substances and the retention values; and 2) calculation to predict retention by summation of the contributions made to it by the individual structural elements of a molecule.

1. Linear Correlations between the Retention Values of Substances and their Molecular Characteristics

An extremely widespread method for the qualitative analysis of substances is the method of homologue identification, in which use is made of linear correlations between the retention of substances and the size of their molecules. This method is based on the linear dependence of the logarithm of the distribution coefficient of the molecules of the substance being studied on the free energy of their reaction with stationary phases. The logarithm of the distribution coefficient of a substance $CH_3(CH_2)X$ is given by [87]

$$\ln K = -\frac{N\Delta G(CH_2)}{RT} - \left[\frac{\Delta G(CH_3)}{RT} + \frac{\Delta G(X)}{RT} + \ln\frac{M_L}{RTd_L}\right], \qquad (6)$$

where $\Delta G(CH_2)$, $\Delta G(CH_3)$, and $\Delta G(X)$ are the standard molar Gibbs free energies of sorption for the transfer of the pure sorbate between states of unit fugacity (gaseous phase) and infinite dilution in the sorbent (stationary phase) for the groups CH_2, CH_3, and X respectively; M_L the molecular weight of the stationary phase; N the number of methylene groups in the molecule of the substance; T the absolute temperature of the experiment, K; R the universal gas constant; and d_L the density of the stationary phase. Since homologues differ from one another only in the values of N, the existence of a linear correlation between $\ln K$ and N in homologous series is obvious.

In the qualitative analysis of homologues, use is made of a logarithmic relationship of the general form:

$$\lg R = a \cdot n + b, \qquad (7)$$

where R is the corrected retention time or volume, or specific or relative retention volumes (the equation remains applicable if the retention index is taken instead of $\lg R$); a a constant characterising the energy of the interaction of the CH_2 group with the sorbent; b a constant characterising the energy of the interaction of the functional groups with the sorbent†; and n the number of carbon atoms in the molecule.

Attention was first drawn to the existence of this correlation by James and Martin[3] for the case of carboxylic acids. The linear relationship naturally still holds if in Eqn.(7) the number of carbon atoms n is replaced by the number of CH_2 groups [101-103] or the molecular weight [104,105]. The retention index of the higher members of homologous series increase by 100 units for every CH_2 group [40,93,106]. The correlation was subsequently confirmed by many workers for various homologous series (the literature has been reviewed [1]).

† Hoshikawa, Kuriyama, and Yamabe [100] give the detailed significance of the constants for the case where the retention is expressed in the form of Kovats' logarithmic indices.

The linearity of the correlation is observed most accurately in the case of non-polar stationary phases, where a decisive factor in the interaction is the dispersion forces, which increase with increase in the size of the molecule. Some deviations from linearity are observed for the first members of the homologous series, particularly on polar stationary phases. Thus the increment in the retention indices, corresponding to one $-CH_2$ group, is rigorously equal to 100 for hydrocarbons only beginning from the seventh member of the series [107]. On polar stationary phases, this increment is lowered, as a consequence of the increase in the contribution to the total energy of the interaction from the partial excess free energy of mixing, which changes in the opposite direction to the molar free energy of condensation [108].

The distortion of the linearity of Eqn.(7) is also influenced slightly by the odd or even character of the number of carbon atoms; the magnitude of this influence can be taken into account [109].

The linear correlation between the free energy of solution and the molecular characteristics is universal, and can be extended to the dependence of the free energy on the number of other atoms or repeating structural units in the molecules of the substances in homologous series—silicon [110], sulphur [111], nitrogen, and oxygen [112,113] atoms, benzene rings [114], $-CH_2-CH_2-NH$ groups [112,113], double bonds [115,116], etc. The relationships between the retention values and the numbers of atoms or groups of the same kind in molecules are justified from the viewpoint of set theory, since both variables take denumerable sets of rational values [117]. Mathematically, these relationships are expressed in the most general form by linear-fractional equations (as revealed in the deviation from linearity of the correlation observed for more accurate measurements over a sufficiently wide range of values [107,118]), which are readily transformed into linear equations. The straight lines obtained for individual classes of substances form a pencil of lines.

Methods related to the group being considered are those based on the correlation between the energy of intermolecular interaction and the molar volume or polarisability of the substance. The energy of the dispersion interaction of an atom i of a substance with a stationary phase U_i can be calculated from the equation [119]

$$U_i = 0.9\pi h\nu \frac{\alpha\rho}{(r+r_f)^3}, \qquad (8)$$

where ν is an average frequency characterising the atom i and the stationary phase; α the polarisability of the atom i of the substance being analysed; ρ the density of the polarisability of the stationary phase; and r and r_f the average van der Waals radii of the atoms of the substances being analysed and the functional groups of the stationary phase respectively.

Since the volume of a molecule is proportional to the cube of its van der Waals radius, and the ratio of the polarisability to the molecular volume is in turn a function of the coefficient of refraction, the energy of the intermolecular interaction, and hence the retention value of the substance in the stationary phase, show a correlation with such physicochemical characteristics of the molecules as the parachor, density, coefficient of refraction, molar refraction, dipole moment, etc.

In fact, a number of authors have demonstrated and used for qualitative analysis the relationship between the retention parameters on the one hand and the dipole moments [120,121], density [122,123], coefficient of refraction or

molar refraction[124,125,126], the parachor[127], heat of formation[128], and other molecular characteristics[122] on the other. The existence of correlations with other physicochemical characteristics which take denumerable sets of rational values is to be expected.

For example, one group of identification methods is based on the relationship between the retention values and the saturated vapour pressures or boiling points of substances. Since there is a logarithmic relationship between V_g and the saturated vapour pressure p^0,[129,130] a correlation should also be expected between the boiling points $t_{b.p.}$ and the logarithms of the retention values of substances. This correlation cannot be strictly linear, since the dependence of the boiling points on the numbers of carbon atoms in a homologous series is non-linear, but the relationship for I or $\lg V_g$ is close to linear. The correlation is closer to linearity, the greater the similarity in the nature of the forces of intermolecular attraction which are responsible for the interaction between the molecules of the pure substance and between the molecules of the substance and the molecules of the stationary phase[131]. This requirement is satisfied most frequently when the substances being analysed and the stationary phase are similar in character. The relationship

$$\lg R = a(t_{b.p.} + b) \qquad (9)$$

is most frequently used in analyses on non-polar stationary phases, but the linearity is also preserved on polar columns[132,133]. In general, the linearity of the correlation is improved if a term including the activity coefficients of the substances being separated is included in Eqn.(9).[134]

In addition to the correlation (9), other equations including the boiling point have been proposed. Thus Zhukhovitskii and coworkers[135] and Sen[136] proposed the use of the independent parameter $T_{b.p.}/T_{col}$ for the identification of substances. The linear relationship between V_R and $T_{b.p.}/T_{col}$ makes it possible not only to determine the boiling point but also to estimate, from the slope of the straight line, the series to which a given substance belongs[137]. Another dimensionless parameter for the identification of related compounds, independent of the temperature of the analysis and the stationary phase, has been introduced[138]:

$$\varphi_T = \frac{\lg V^0_{R_i} - \lg V^0_{R_1}}{\lg V^0_{R_2} - \lg V^0_{R_1}} = \frac{T_{b.p._i} - T_{b.p._1}}{T_{b.p._2} - T_{b.p._1}}; \qquad (10)$$

where V^0_{Ri}, $V^0_{R_1}$, and $V^0_{R_2}$ are the corrected retention volumes; and $T_{b.p.i}$, $T_{b.p._1}$, and $T_{b.p._2}$ the boiling points of the unknown substance and two known substances respectively. A series of empirical equations for determining boiling points from retention data has been proposed by Japanese workers[139-142].

Bach and coworkers[143], from the dependence of t_R on the vapour pressures of substances, introduced the "retention boiling point" to supplement Kovats' system of retention indices. For correctly chosen operating conditions, this boiling point is fairly close to the true boiling point. All the above correlations make it possible to use the retention value to determine approximately the boiling point of a substance and hence to use tables of the boiling points of substances for identification.

Some authors ascribe considerable importance to the dependence of the retention values on the temperature of analysis T. The relationship between $\lg V$ and the reciprocal of the absolute temperature is linear[12]

$$\lg V = A + B/T. \qquad (11)$$

An analogous relationship holds for the relative retention characteristics[144]. It was later found that the correlation between I and $\lg V$ or I [145,148] is given more accurately by an equation which is analogous to the Antoine equation, describing the temperature dependence of the saturated vapour pressure of a substance:

$$\lg V_g \text{ or } \lg I = A' + \frac{B'}{T + C'}. \qquad (12)$$

In the temperature range characteristic of gas chromatography, the almost linear part of the hyperbola is used[144,146]. The coefficient A is directly related to the entropy, and the constants B [in Eqn.(12)] and also B' and C' are related to the enthalpy of solution. Since the thermodynamic functions of solution are characteristic for each substance and are different for different homologous series, the correlations (11) and (12) can be widely used for the identification of substances. The $\lg R - 1/T$ straight lines for the members of a given homologous series intersect at a characteristic point, the position of which is independent of the nature of the stationary phase[149].

Various non-linear equations characterising the temperature dependence of the retention indices have also been proposed[150,151]. The fruitful application of this method for the qualitative analysis of compounds of different classes has been demonstrated by a number of workers[12,103,126,149,150,152-155].

A characteristic parameter for the identification of substances is the temperature coefficient of the retention indices dI/dT. The values of this coefficient are different for groups of substances having different degrees of saturation or branching and also for cyclic compounds[156-158]. Saha and Mitra[159-161] showed that dI/dT for each series of hydrocarbons is constant and decreases in the order: aromatic hydrocarbons > cyclo-alkanes > tetra- and trialkylalkanes > di- and monoalkylalkanes. The temperature coefficients of the retention indices are linearly related to the mean square radii of the molecules of isomeric alkanes[162]. A thermodynamic treatment of the temperature coefficients of the retention indices has been given by Hammers and de Ligny[163].

Thus a number of correlations have been proposed for the gas chromatographic identification of separated substances using a single column. They have been widely used up to the present, but since the constants of the correlation equations are empirical, the validity of the correlations for individual classes of substance must be proved experimentally. To construct the corresponding curves, it is necessary to have at least three representatives of a series. After the construction of the correlation graphs, the identification of homologues does not present serious difficulty.

In addition to correlations between the physicochemical characteristics of substances and the retention values on a single stationary phase, corresponding correlations determined on two or several columns of different polarity are widely used in qualitative analysis. The values of $\lg R$ obtained on several columns show a correlation with one another. The graphs for substances belonging to different homologous series lie in different regions of the corresponding diagrams. Thus the values of $\lg R$ obtained on two columns of different polarity for each homologous series of substances lie on straight lines parallel to one another[164]. If R is plotted directly on the graph instead of $\lg R$, the homologues lie on straight lines having a characteristic slope. A correlation of this kind was

first used for the identification of primary, secondary, and tertiary alkylamines[165]. The method was subsequently widely recommended for the identification of organic substances of different classes[4,29,111,164,166-170]. Since many pairs of columns, for series of substances, give straight lines which are situated extremely close of one another on the graph, the identification requires a careful choice of sorbents[169,170].

A significant discovery was the detection[171] of the "roofing tile effect", that is that the values of $\lg V_R$ or I for isomeric compounds, obtained on two columns of different polarity, lie on parallel lines, forming "roofing tile groups" in accordance with the number of primary, secondary, tertiary, and quaternary carbon atoms in the molecules. This effect makes it possible to use gas chromatographic retention data on two columns to determine the fine structure of organic molecules. Moreover, the difference in the retention indices on two columns having sorbents with different polarities gives information on the nature of the functional groups[40,45].

Brown[6] proposed the measurement of the retention of substances on three columns, containing stationary phases with different electronic characteristics—non-polar, electron-donor, electron-acceptor. If the data are expressed as retention fractions ("affinity fractions") and plotted on a triangular diagram, each substance is represented by a point, according to its donor-acceptor properties. The points corresponding to substances in a given homologous series lie on straight lines, which are directed towards the apex corresponding to the non-polar column. This method has been used to identify steroids[172], ethers, nitriles, and aldehydes[173], alcohols and esters[174,175], aromatic hydrocarbons and ketones[175], and nitrogen-containing bases[176,177]. Brown's method can also be used to estimate the donor–acceptor properties of stationary phases[172] and to determine the optimum composition of binary stationary phases[178].

Ladon and Sandler[179] put forward an equation for determining the number of carbon atoms in a substance being analysed from its retention times on three carefully selected phases; the coefficients of the equations were found by regression analysis. The correlation is based on the use of one or several columns, depending on the complexity of the problem. Correlations using several columns are employed more frequently for the group analysis of substances.

2. Calculations for Predicting Retention Values

The subsequent development of the method using the correlation between gas chromatographic data and the structures of substances has involved the development of the so-called predictive calculation, in which the retention values on a given column or pair of columns are predicted from an assumed structural formula, and the qualitative analysis is carried out by comparing the calculated value with the experimental value for the component of the mixture being studied. Calculations for predicting retention form the subject of a large number of original papers and several reviews[47,180-182].

a) Calculation of the retention values from the physicochemical properties of the sorbates and stationary phases

The retention of a substance in a chromatographic column is determined by the free energy of the intermolecular interaction in the sorbent–sorbate system; it is therefore possible to predict retention values from empirical relationships between this energy and the physicochemical characteristics of the substances being analysed and the stationary phases.

The distribution coefficient and specific retention volume are inversely proportional to the product of the saturated vapour pressure of the substance being analysed at the temperature of the column and the activity coefficient[183]; a knowledge of these quantities makes it possible to predict the retention. The empirical calculation of activity coefficients from the general theory of solutions has been described[184]. This calculation is tedious, however, and makes it possible to estimate the activity coefficient only approximately. It is more convenient to use the relative values based on the following equation[185]:

$$\frac{\lg V_{R_2}}{\lg V_{R_1}} = \lg\left(\frac{p_1^0}{p_2^0}\right) + \lg\left(\frac{\gamma_1^0}{\gamma_2^0}\right), \qquad (13)$$

where γ_1^0 and γ_2^0 are the activity coefficients of substances 1 and 2 dissolved in the stationary phase. If the substances belong to the same series, $\gamma_1^0 = \gamma_2^0$ and Eqn.(13) is simplified[186].

The retention index of hydrocarbons on hydrocarbon stationary phases is given by[187]:

$$I = 100\,\frac{\lg\left(p_n^0 \cdot V_{\mathrm{mol}_n}/p_x^0 V_{\mathrm{mol}_x}\right)}{\lg\left(p_n^0 \cdot V_{\mathrm{mol}_n} p_{n+1}^0 V_{\mathrm{mol}_{n+1}}\right)}, \qquad (14)$$

where p_x^0, p_n^0, and p_{n+1}^0 are the saturated vapour pressures of the substance being studied and n-alkanes containing n and $n+1$ carbon atoms; and V_{mol_x}, V_{mol_n}, and $V_{\mathrm{mol}_{n+1}}$ the molar volumes of the substance and n-alkanes containing n and $n+1$ carbon atoms.

Several equations have been proposed for the theoretical calculation of the heats (or free energies) of solution. Sakharov[119] showed that the heat of formation ΔH_S of a solution at infinite dilution is made up of the energy of interaction of the sorbate with the sorbent (equal to the difference in the energies of the dispersion interaction of the atoms of the substance with the stationary phase, U_i, and the dispersion interaction of the atoms of the substance with the molecules of the stationary phase which might have occupied the space blocked by the other atoms of the molecules of the substance, E_i) and the energy of formation, in the stationary phase, of cavities having shapes and sizes corresponding to those of the sorbate molecule (this energy is proportional to the surface area of the molecule of the substance S and the surface tension of the solvent σ):

$$\Delta H_s = -\sigma S + \Sigma U_i - \Sigma E_i. \qquad (15)$$

The value of U_i for spherical molecules is determined from Eqn.(8), and ΣE_i, if the polarisability densities of the stationary phase and the sorbate are similar, can be replaced by twice the energy of the dispersion interaction between the atoms of the molecule of the sorbate $2E_S$ (that is by the magnitude of the steric effect)[119]. The method has been used successfully to calculate the retention of acyclic saturated[119], unsaturated[124], and aromatic[118] hydrocarbons, and also amino-substituted pyridines, quinolines, and thiophenes[188] on non-polar or weakly polar stationary phases.

Various modifications of the general Eqn.(15) have been proposed, with more accurate allowance for the energy of formation of a hole in the case of planar molecules of the stationary phase[189] or with an expression for

the energy of the London dispersion interaction [190-192]. These equations [190-192], together with the interaction of non-polar substances, have also been used to estimate the interaction of polar sorbates with non-polar stationary phases. The identification of substances reduces to the theoretical calculation of the heats of solution and comparison of the results with the experimental values found from the temperature dependence of $\lg V_R$.

The proportion of polar interactions in a column is also characterised by the dielectric constant of the stationary phase ϵ. A method has been proposed for predicting the retention of a substance on any stationary phase, based on the linear relationship between $\lg V_g$ and $1/\epsilon$. [193] If the substance being analysed and the stationary phases are polar, the retention volumes in the general case can be written as the sum [194]:

$$\lg V_R = \lg V_R^A + pP, \quad (16)$$

where V_R^A is the retention volume of the substance on the non-polar stationary phase, p the polarity of the substance being analysed, and P the polarity of the stationary phase.

The value of V_R^A can be calculated from the above equations, or determined experimentally; the polarities p and P can also either be estimated from the dipole moments, dielectric constants, or other physical quantities, or found experimentally from gas chromatographic data.

A procedure for predicting the retention from the gas chromatographic characteristics of sorbates and stationary phases was developed by Rohrschneider [195-199], who used a so-called linear combination of forms of interaction, based on the additivity of the free energy of solution [197]:

$$\Delta G = \Delta G_A + \Delta G_B + \ldots + \Delta G_Z, \quad (17)$$

where ΔG is the total free energy of solution; and $\Delta G_A \ldots \Delta G_Z$ the proportions of the free energy of solution corresponding to the different forms of intermolecular interaction from A to Z. The proportions of the free energy of solution represent the product of a factor characterising the ability of the stationary phase to undergo interaction of a definite type and a factor characterising the ability of the substance to undergo the same type of interaction.

Initially, Rohrschneider took account of only the dispersion interaction with the π-electrons of the aromatic ring, donor–acceptor interaction with the formation of a hydrogen bond, and the orientation of dipoles [195,196]. Subsequently, the calculation was improved by taking account of electron-acceptor and proton-donor interactions [197-199]. The retention of a substance, in the form of the relative retention volumes or times, is obtained by taking account of six types of interaction, or in the form of I or ΔI by taking account of five types of interaction [195,198]. For any substance on an arbitrary stationary phase

$$\Delta I = ax + by + cz + du + es, \quad (18)$$

where ΔI is the difference in the retention indices on polar and non-polar stationary phases; a, b, c, d, e, are constants characterising the substance being separated; and x, y, z, u, and s are constants characterising the stationary phases. The constants x, y, z, u, and s are determined from the difference in the retention indices, on the column being studied and on squalane, of substances characterising the types of interaction listed above (benzene, ethanol, butan-2-one, nitromethane, and pyridine) [198, 199], and the constants a, b, c, d, and e from the difference in the retention indices of the substance being studied on a non-polar sorbent and on stationary phases characterising the principal types of intermolecular interaction [199].

The subsequent development of Rohrschneider's method has involved an increase in the number of standard substances for characterising stationary phases and sorbates in order to make more detailed allowance for the interactions [200], and also a decrease in the number of standard substances by combining standards characterising similar types of interaction [201-203]. Appropriate mathematical methods have been developed for each of these approaches. Weiner and Howery [204,205] showed by factorial analysis that for an adequate description of a sorbate–sorbent system it is sufficient to have eight terms in an equation of type (18) to the five types of interaction it is necessary to add the Lewis acidity, the Lewis basicity, and the entropy [206]. Lowry and coworkers [207], using the "nearest neighbour" method, showed that satisfactory results in the prediction of retention can be obtained using four functional tests characterising the principal types of interaction.

The above methods are semi-empirical, and require a fairly large expenditure of time for the determination of the corresponding constants. In addition, the values found are not completely unambiguous.

b) Calculation of retention values from structural element increments

An extremely fruitful approach in qualitative analysis by predictive calculations is the development of methods based on the additivity of the enthalpies and free energies of solution of a substance in stationary phases. The interaction of any substance with a sorbent, determining its retention, represents the sum of the interactions of the separate parts of the molecule. By determining the increments in the retention values for all the structural elements of a molecule, it is possible to predict the chromatographic behaviour of the molecule as a whole. Since the enthalpy of solution is linearly related to $\lg V_R$, [12] additivity of the increments can be expected only if the retention data are expressed on a logarithmic scale. The identification of homologues from linear correlations, based on this principle, was examined in the previous section.

The additivity of the increments in retention values characteristic of the structural elements of molecules was first demonstrated on the basis of Kovats' system of retention indices [40,93,106,208]. In addition to the fact that the contribution of the $-CH_2-$ group to the retention value is constant, which formed the basis of the linear correlation methods examined above, it was established that the introduction of a given group of atoms into the molecules of compounds having analogous structures changes the value of the retention indices by the same amount. Assuming that the dispersion interactions of parts of molecules with different stationary phases are equal, Kovats proposed that the specific interactions of the molecules with a sorbent be characterised by increments ΔI, calculated from the difference in the values of the retention indices of the substances on polar and non-polar stationary phases. The increments ΔI consist of a principal term taking account of the influence of the "characteristic zone" (functional group, double bond, ring, etc.), and corrections taking account of the influence of the surroundings of this zone. Unknown compounds are identified by comparing the experimentally determined value with the values of ΔI calculated from several assumed structural formulae.

In 1962, Swoboda [209] suggested that the chromatographic behaviour of substances could be characterised more effectively by subtracting from their retention indices the

retention indices of the n-alkanes making up the main framework of the molecule. Since the difference obtained characterises the contribution of the functional groups to the retention, Swoboda called it the "functional retention index".

These ideas were later developed by Schomburg [47,52,210-217], who suggested that the difference between the retention indices of the substance and the alkane having an analogous carbon framework (the homomorph) be called the homomorphic factor H. [211] The homomorphic factors are extremely sensitive to changes in the geometry of a molecule—branching, the position of a double bond, and configuration—whereas the values of ΔI are not very characteristic in this respect [212,213]. The difference in the homomorphic factors on polar and non-polar columns ΔH, characterises the influence of the specific forces of intermolecular interaction [47,213]. The values of H, ΔI, and ΔH are additive, but the additivity breaks down if two characteristic structural elements are in close proximity. In these cases, Schomburg proposes the introduction of a correction in the form of increments of second order [215,216], which, like the corrections of Kovats and Wehrli [40,93,208], take account of the interaction of groups and the steric and other effects of the environment. The applicability of the principle of additivity of the increments in the retention indices for predicting the chromatographic behaviour of substances [210-217] has been confirmed by a number of workers for various classes of compound [103,218-224].

Since I and ΔI depend on temperature, they must be compared for identical temperatures, or recalculated [147]. A number of authors [147,225,226] have suggested that ΔI values be related to 0 K. At the absolute zero, when the thermal energy of a substance is equal to zero, the factors corresponding to the interaction between substances and stationary phases are more rigorous characteristics, depending only on the structural characteristics of the substances.

If the retention indices are expressed on the molecular weight scale (so-called effective molecular weights), substances in homologous series can be identified using the constancy and additivity of the increments in the molecular weights ΔM_e (the difference between the true and effective molecular weights) [37,39], as in the case of ΔI. Finally, instead of using ΔI, ΔH, and ΔM_e, retention values can be predicted by using directly the increments in the partial molar standard enthalpy $\Delta\bar{H}^0_S$ and entropy $\Delta\bar{S}^0_S$ of solution, characteristic of the individual structural elements of molecules [227]. They are less dependent on temperature than the increments ΔI, ΔH, and ΔM_e, and this makes it possible to calculate V_g over a wide temperature range, using the values of $\Delta\bar{H}^0_S$ and $\Delta\bar{S}^0_S$ measured at a given temperature.

Most of the works cited demonstrate that ΔI, ΔH, and ΔM_e are constant in homologous series, but more accurate measurements of these quantities over a sufficiently wide range show that they depend slightly on the number of carbon atoms in the group. The dependence is described effectively by the equation of a linear-fractional function

$$\Delta I = \frac{n}{an+b}, \qquad (19)$$

which can be transformed into the straight line equation [117]

$$Y = an + b \quad \text{for} \quad Y = n/\Delta I.$$

The principle of additivity of ΔI, H, ΔH, and ΔM_e, and its use for the identification of substances, are also justified by set theory.

The identification of substances by predicting retention from molecular structure is also possible using logarithmic interpolation. This method was developed by Evans and Smith [32], who showed that the retention time $t_{R_{1,2}}$ of unsymmetrical compounds of the type RXR′ can be determined if the retention times $t_{R_{1,1}}$ and $t_{R_{2,2}}$ for the symmetrical substances RXR and R′XR′ respectively are known. The equation which they proposed,

$$\lg t_{R_{1,2}} = \frac{1}{2}(\lg t_{R_{1,1}} + \lg t_{R_{2,2}}) \qquad (20)$$

is applicable if the active group X is not sterically shielded and is not included in a conjugated system of multiple bonds, and if the other parts of the molecule R and R′ are not highly polar.

The linear-fractional dependence of $\lg V_R$ on the molar refraction of the stationary phase has been made the basis of a method for predicting retention for substances of a given homologous series on any stationary phase if the values of V_R for this series on two stationary phases are known [228].

A general approach to the problem of predicting retention by calculation based on the additivity of the contributions of structural elements was developed by Berezkin [229-233], who showed that all the above relationships are particular cases of the general relationship [229,230]

$$\lg R = \sum_{i,j}^{k} n_{ij} P_{ij}, \qquad (21)$$

where P_{ij} is the contribution of a given structural element to $\lg R$; and n_{ij} the number of structural elements in the molecule of the substance. The structural elements on which the calculation is based may be either atoms or bonds, since the accuracy of the calculations depends not on the fundamental differences between the atoms and the bonds, but on the detail with which they are classified [234,235]. As the structural elements for the calculations, Berezkin took the bonds, with allowance for the first-order environment. If allowance is made for a larger environment, it is possible in principle to obtain more accurate results, but the error in the determination of the experimental data makes this calculation inappropriate. It is more justified and convenient in practice to carry out the predictive calculation of t_R^{rel} from an equation which contains an additional constant P_0, which depends on the choice of standard substance [233]:

$$\lg t_R^{rel} = P_0 + \sum_{i,j}^{k} n_{ij} P_{ij}. \qquad (22)$$

Relative or absolute values of R have been calculated for alkanes [229,230], alkenes [232], esters [230], amines [233], alcohols, ketones, sulphides, and various oxygen- and nitrogen-containing heterocyclic compounds [236].

Berezkin's approach has been made the basis of a predictive calculation of the retention indices of substances [237]. The influence of the environment is taken into account [237] not as different versions of the bonds [232] but as a separate component Π:

$$I = \sum_{i,j} I_{ij}^{(1)} + \Pi, \qquad (23)$$

where $I_{ij}^{(1)}$ represents the contributions of the individual bonds and structural elements to the retention indices of

the mono-functional compounds, and $\Pi = \sum_{ij}\pi_{ij}$ is the contribution of the interaction, which takes maximum values for 1,2-substitution.

It has also been shown that it is necessary and possible to take account of the inductive effect, which is estimated in the form of the coefficients of a multiple regression equation [238]. The dependence of the contributions of the structural elements and their sensitivity to the inductive effect on the nature of the structural elements and on the dielectric constant of the stationary phase has been studied [239,240].

In a series of papers [241-249] devoted to the predictive calculation of retention indices from the additivity of the contributions of the structural elements of molecules, the latter were dealt with in even more detail. The retention index of a substance was represented as the sum of three components [241-243]:

$$I = I_a + I_b + I_i = I_M + I_i, \qquad (24)$$

where I_a, I_b, and I_i represent respectively the contributions made to the retention index by the atoms, the bonds, and the interaction between the substance and the stationary phase. The atomic component of the retention index I_a is found as the sum of the indices of all the atoms of the molecule, which in turn are approximately equal to the atomic weight of the element divided by 10. [242,243] The component I_b is equal to the sum of the contributions from all the bonds of the molecule; the contributions of the bonds are determined with allowance for the immediate environment, by iteration. These two terms make up the part of the retention index which is characteristic of the given substance and independent of the nature of the stationary phase and temperature. This part of the retention index, called the molecular component I_M, can be calculated from the structural formula of a substance.

The interaction of a substance with a stationary phase, and its dependence on the temperature of the analysis, are taken into account by the component I_i. Experimental data [243] show that for homologous series of substances on squalane, $I_i = 4.97\,yI$ (y is a coefficient characteristic of a given class of substance; for example, for alkanes, $y = 0.15$ [241]). For other stationary phases, it is suggested that the component of the interaction I_i (or the interaction factor $F_i = I_M/I$) be further divided into two parts: I_{ia}, the contribution of the average interaction, and I_{ii}, the contribution of the individual interaction [242,244]. I_{ia} characterises the dispersion interactions, and I_{ii} the specific interactions between the molecules of the substance being analysed and the stationary phase. $I_{ia} = 0.7455.I$, [244] but I_{ii} must be determined by the methods of Rohrschneider [197-199,244] or McReynolds [200,245,246] (on a non-polar sorbent, $I_{ii} = 0$, $I_i = I_{ia} = 0.7455.I$ [249]). The method is also applicable when corrected retention volumes are used instead of the retention index [248].

The predictive calculation system developed by Takacs represents a theoretical approach to the separate determination of all the factors making up the retention index. This approach makes it possible to understand more deeply the nature of the retention of substances in chromatography and to distinguish the factors responsible for the gas chromatographic behaviour of substances in specific examples of analysis. Although the method is undoubtedly of considerable value, the determination of such important components of the retention index as I_b and I_{ii} is still semi-empirical. Moreover, the method for determining I_b is not given, so that the calculation is not reproducible [250], particularly for cyclic compounds. For practical purposes, it is much more convenient to use the method of calculation proposed by Berezkin, which, although it does not contain the details of P_{ij}, makes it possible to use definite experimental material to find unambiguous values of the contributions of the structural elements for the predictive calculation of the retention of other substances.

Thus the methods of incremental calculation provide theoretically justified and extremely promising methods for the qualitative gas chromatographic analysis of organic substances. Their use facilitates to a considerable extent the solution of problems arising when gas chromatography is used as an analytical method.

c) Prediction of retention values from a molecular-statistical calculation

The most general solution of the problem of predicting retention values by calculation is the theoretical molecular-statistical calculation of the specific retention volumes and Henry coefficients. This quantitative approach is being successfully developed in the USSR by Kiselev, Poshkus, and Afreimovich [251-259] for the gas-adsorption chromatographic characteristics obtained at sufficiently high temperatures with the assumption that the intramolecular vibrations of the adsorbent remain unchanged on adsorption [257]. Henry's coefficient K_1 (the specific retention volume for zero degree of covering of the surface of the adsorbent V_ρ) for three-dimensional quasi-rigid molecules is given by the following equation [256, 259]:

$$(V_\rho)\,K_1 = \frac{1}{8\pi^2 S}\int \{\exp[-\Phi(x, y, z, \vartheta, \varphi, \psi)/kT] - 1\}\sin\vartheta\, dx\, dy\, dz\, d\vartheta\, d\varphi\, d\psi, \qquad (25)$$

where S is the surface area of the adsorbent; Φ the potential energy of the adsorbate–adsorbent intermolecular interaction, which depends on the coordinates of the centre of mass of the molecule x, y, z and the angles of its orientation relative to the surface of the adsorbent θ, φ, ψ; and k the Boltzmann constant.

The potential energy of the intermolecular interaction is determined as the sum of the energies of the paired interactions over all interacting atoms, expressed in terms of the atom–atom potential functions of intermolecular interaction $\varphi_{C\ldots A}$ (or the atom–group potential functions in the case of the study of complex molecules). The atom–atom potential functions are calculated using the familiar semi-empirical equations for the Buckingham–Korner or Lennard-Jones potentials; the constants of the equations are calculated by the method of Kirkwood and Miller [260,261]. This method has been used to calculate the Henry coefficients for the noble gases and nitrogen for adsorption on graphitised thermal carbon black [251,253,258] and various cationic forms of zeolite A. [262,263] The molecular-statistical calculation of the Henry coefficients for adsorption on graphitised thermal carbon black was carried out for the C_1–C_6 n-alkanes [255-259]; the effective atom–atom potentials of the intermolecular interaction $\varphi_{C\ldots C}$ and $\varphi_{C\ldots H}$ were calculated using a special constant factor [256,259]. Using the effective potential functions of the atom–atom interaction and taking account of the differences in the adsorption of the rotational isomers of the n-alkanes, the authors cited obtained the values of V_ρ, K_1, and $\lg K_1$, and the dependence of the latter on the reciprocal of the absolute temperature, in good agreement

with experimental data. In the case unsaturated and aromatic hydrocarbons, it was necessary to introduce into the potential functions $\varphi_{C...C}$ additional factors taking account of the stronger interaction between the graphitised carbon black and carbon in other valency states (compared with the n-alkanes and cycloparaffins). In principle, by taking account of the differences in the valency states of carbon in molecules, it is possible to calculate the Henry coefficients or retention volumes for any hydrocarbons on graphite.

Molecular-statistical calculations have also been carried out for the adsorption of neopentane by NaX zeolite[264] and the adsorption of ethane by the zeolites NaX and NaY.[265]

The molecular-statistical calculation of retention values using semi-empirical potential functions is at present the most well-founded theoretical approach to the solution of the problems of qualitative analysis in gas chromatography. The chief disadvantage of the method is the tedious character of the calculations, and also the semi-empirical character of various constants in the equations used; the calculation of these constants requires many assumptions. This disadvantage can be overcome, however, using modern computing techniques. Unfortunately, at the present time the possibilities provided by molecular-statistical calculations are restricted to several examples of gas-adsorption chromatography on the fairly uniform surfaces of crystalline adsorbents. Since the structure of liquids has not yet been sufficiently fully studied, molecular-statistical calculations in gas-liquid chromatography represent a task for the future.

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The Use of Spin-trapping in the Study of the Mechanisms of Radical Processes

V.E.Zubarev, V.N.Belevskii, and L.T.Bugaenko

The review is devoted to the spin-trapping method developed in recent years and used to identify short-lived radicals (mainly in liquid phase) and to investigate the mechanisms of their reactions. Unstable radicals are accepted by a spin-trapping agent with formation of a fairly stable free radical which carries information about its short-lived precursor. The EPR spectra of the resulting spin adducts can be recorded in the liquid phase and are as a rule well resolved. The properties of various spin-trapping agents are described in detail and tables of the parameters of the EPR spectra of the adducts of spin-trapping agents with the trapped radicals are presented. The application of the spin-trapping method in the study of the mechanisms of radical processes in various fields of chemistry is considered.
The bibliography includes 161 references.

CONTENTS

I.	Introduction	729
II.	Spin-trapping agents	730
III.	The application of spin-trapping agents in the study of radical processes	737

I. INTRODUCTION

The free radicals arising in the course of chemical reactions usually have very short lifetimes, which precludes their detection in the chemical reaction zone by the usual EPR method, since the steady-state concentrations of the radicals are below the sensitivity of modern EPR spectrometers. In order to detect short-lived radicals, special research techniques have therefore been developed: (1) stabilisation of radicals in the solid phase at low temperatures; (2) flow methods in the liquid phase with the radicals generated by means of Fenton's reagent or the titanium reagent in an acid medium; (3) recording of EPR spectra (or optical absorption spectra) under continuous irradiation by an electron beam or light in the liquid phase directly in the resonator; (4) stabilisation of radicals on the surface; (5) the method of chemically induced dynamic nuclear polarisation (CIDNP). These methods yielded much information about the radicals and the mechanisms of radical reactions. However, they suffer from many significant limitations. Owing to the high rate of radical reactions, it is usually impossible to detect the primary radicals. Analysis of the EPR spectra of solid specimens is in most cases difficult because of the broadening of the lines and the superposition of the spectra of several radicals. Flow methods are suitable only for a limited number of chemical reactions and involve the consumption of a large amount of reagents. Considerable technical and methodological difficulties arise also when the CIDNP method or a spectrometer irradiated by an electron beam are used. The majority of radical reactions occurring in the liquid phase cannot be investigated by the methods enumerated above.

The spin-trapping method, developed in recent years, has significantly greater possibilities and permits the investigation of short-lived radicals in liquid, solid, and gaseous phases. It is based on the acceptance by compounds (spin-trapping agents) of short-lived radicals with formation of fairly stable radical adducts having a characteristic EPR spectrum. Extensive information about short-lived radicals arising in photolysis, radiolysis, electrolysis, gas discharge, oxidation, thermal decomposition, rearrangement, and polymerisation has been obtained with the aid of the spin-trapping method. The aim of the present review is to demonstrate the possibilities of the method and the prospects for its utilisation in the study of the mechanisms of radical reactions. Earlier reviews[1-3] present data published up to 1971†. Since then the number of studies involving the use of spin trapping agents has greatly increased, new spin-trapping agents have become available, and new fields of their application have arisen.

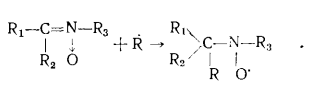
II. SPIN-TRAPPING AGENTS

Mainly nitroso-compounds and nitrones are used as spin-trapping agents. In the study of the mechanism of the photolysis of 't-nitrosobutane' and nitrosobenzene it was observed[4] that these compounds react with the intermediate radicals arising as a result of the photolysis of the nitroso-compounds, forming stable nitroxy-radicals. Iwamura and Inamoto[5,6] were the first to use nitrones for the synthesis of stable radicals. It was shown subsequently that many nitroso-compounds and nitrones combine with unstable radicals, forming long-lived radicals. Table 1 presents a list of the main spin-trapping agents.

Nitroso-t-butane and *C*-phenyl-*N*-t-butylnitrone are most frequently employed. The unstable radical adds to the N–O fragment of the nitroso-compound:

$$R_1{-}NO + \dot{R} \rightarrow R_1{-}N(\dot{O}){-}R \quad .$$

Radicals add to the double bond of nitrones:



Nitroxy-radicals, which belong to the large class of stable radicals whose properties have been thoroughly investigated[7,8], are formed in both cases.

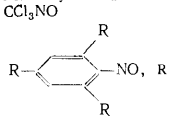
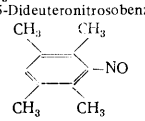
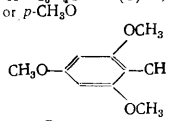
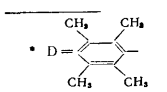
Apart from nitroso-compounds and nitrones, certain other compounds containing multiple bonds or heteroatoms are used as spin-trapping agents (see Table 1).

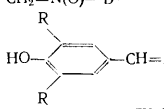
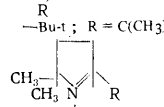
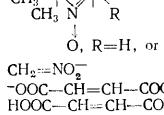
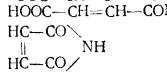
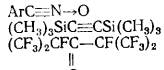
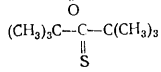
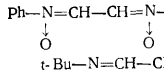
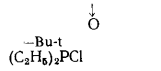
1. Nitrosoalkanes

The majority of nitroso-compounds exist in the forms of dimers which dissociate into monomers in solution. Only the monomeric form reacts with radicals. Mainly t-nitrosobutane and related compounds are used as spin trapping agents.

t-Nitrosobutane (TNB, t-BuNO). The simplest and most convenient method of synthesising TNB has been described by Stowell[9] (oxidation of t-$BuNH_2$ with hydrogen peroxide in the presence of Na_2WO_4), but other methods of synthesis are also available[10]. Solid TNB is a colourless dimer, which dissociates in solution with the appearance of a characteristic blue colour. The dimer–monomer equilibrium constants in CCl_4, methanol, heptane, and toluene have been determined[9,11-14].

Table 1. The spin-trapping agents investigated.

Spin-trapping agent	References
t-BuNO(TNB)	(see Table 2)
$(CF_3)_2CNO$	21, 22
$(CD_3)_2CNO$	23–25
$(CH_3)_2C(NO)C(O)CH_3$	2, 18
$Ph{-}CH(NO){-}CH_3$	15
Nitrosocyclohexane	15
CCl_3NO	31
	41–43
(BNB), CH_3O, CH_3OCO, Cl	(see also Table 4)
C_6H_5NO	19
C_6F_5NO	41
3,5-Dideuteronitrosobenzene	19
	41
	(see also Table 3)
N,N-Dimethyl-*p*-nitrosoaniline	154
PhCH = N(O)-Bu-t (PBN)	(see also Table 5)
p-$XC_6H_4CH{=}N(O){-}$Bu-t X=NO_2, Cl, CH_3, CH_3O	5,68
$PhCH{=}N(O)Ph$	152
$PhCH{=}N(O)C_6H_4X$, X=*p*-Cl, *p*-OCH_3, *p*-CH_3, or *m*-Cl	152
$Ph_2C{=}N(O)Ph$	152
$X{-}C_6H_4CH{=}N(O)Ph$, X=*p*-NO_2 or *p*-CH_3O	152
	156
	

Spin-trapping agent	References
$PhCH{=}N(O)CH_2Ph$	152
$Ph_2C{=}N(O)CH_2Ph$	152
$X{-}C_6H_4CH{=}N(O)CH_2Ph$, X = *p*-$NO_2$, or *p*-$C(CH_3)_3$	152
$PhN(NO){-}C(O)CH_3$	153
$CH_2{=}N(O)$–Bu-t; (MH)	33, 69
$CH_2{=}N(O)$–D*	41
	62
	
	64–68
$CH_2{=}NO_2^-$	76–79
$^-OOC{-}CH{=}CH{-}COO^-$	74, 75
$HOOC{-}CH{=}CH{-}CONH_2$	74, 75
	74, 75
	73
$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$	81
$(CF_3)_2CFC(CF_3)_2$	82
	151
	99
	5
	80

The monomeric form of TNB in solution has an optical absorption maximum at 667 nm (ϵ = 18.2 litre $mole^{-1}$ s^{-1} in methanol[12]), while the dimer absorbs at 294 nm ($\epsilon = 5.7 \times 10^3$ litre $mole^{-1}$ s^{-1} in heptane[14]). The photolysis of liquid TNB solutions by visible light results in the formation of stable t-Bu_2NO radicals[4,15] and the solution cannot therefore be stored in the light. These radicals are also formed on heating TNB solutions[16]. In frozen solutions the monomeric form of TNB is resistant to the action of light[17], while the dimer dissociates under these conditions to the monomer under the influence of light[17,18]. It has been suggested that the photolysis of TNB in solution proceeds via the following mechanism:

$$\text{t-BuNO} \xrightarrow{h\nu} \text{t-BuNO}^* \rightarrow \text{t-Bu}^\cdot + \text{NO}, \quad (1)$$

$$\text{t-Bu}^\cdot + \text{t-BuNO} \rightarrow \text{t-Bu}_2\text{NO}^\cdot, \quad (2)$$

†See also the review by R. Kh. Freidlina, I. I. Kandror, and R. G. Gasanov, Uspekhi. Khim., 47, 508 (1978) [Russian Chemical Reviews, 47, No. 3 (1978)].

or

$$t\text{-BuNO}^* + t\text{-BuNO} \rightarrow t\text{-Bu}_2\dot{N}O + NO. \quad (3)$$

t-$Bu_2\dot{N}O$ radicals are also formed in the radiolysis of TNB solutions in benzene and toluene at 20°C as a result of the transfer of excitation energy from aromatic compounds to TNB.[13]

It has been shown[18] that TNB is stable in the presence of oxidants such as $Pb(AcO)_4$ and Ce^{4+} and over a wide pH range[18]. However, it was later observed[19] that alkyl hydroperoxides and dimethyl sulphoxides react with nitroso-compounds to form nitroxy-radicals:

$$R'OOH + R''NO \rightarrow \underset{\underset{OOR'}{|}}{R''\text{—}N\text{—}OH} \rightarrow R'\dot{O} + \underset{\underset{O\cdot}{|}}{R''\text{—}N\text{—}OH} \xrightarrow{+R''NO} \underset{\underset{O\cdot}{|}}{R'\text{—}O\text{—}N\text{—}R''}. \quad (4)$$

Nitroso-compounds react readily with certain anions [polystyrene, poly(methyl methacrylate), nitromethane, acetate, and cyanide anions][20], forming amino-oxyanions, which are oxidised either by the nitroso-compound itself or by "traces" of O_2 to nitroxy-radicals:

$$R^- + t\text{-BuNO} \rightarrow t\text{-Bu}\underset{\underset{O^-}{|}}{\text{—}N\text{—}R} \xrightarrow{t\text{-BuNO}} R\text{—}\underset{\underset{O\cdot}{|}}{N\text{—}}Bu\text{-}t. \quad (5)$$

Table 2. Parameters of the EPR spectra of the TNB radical adducts.

Radical	Solvent	T, °C	a_N, G	a^H_β, G	a^H_γ, G	Refs.
$\dot{H}$	Methanol	−50	13.5	13.5	—	27
$\dot{H}$	Benzene	+20	13.6	12.9	—	28—30
$\dot{C}H_3$	CH_2Cl_2	−70	15.5	12.9	—	18
$\dot{C}H_3$	DMSO + H_2O	+20	16.0	13.2	—	31, 32
$\dot{C}H_3$	Benzene	+20	15.2	11.3	—	33
$CH_3\dot{C}H_2$	CH_2Cl_2	−40	14.9	10.4	0.5	18
$CH_3\dot{C}H_2$	DMSO + H_2O	+20	15.7	11.3	0.3	32
$C_5H_{11}\dot{C}H_2$	Water	+20	15.0	10.4	0.5	32
$C_2H_5(CH_3)\dot{C}H$	CH_2Cl_2	−40	15.3	2.2	—	18
$(CH_3)_2\dot{C}H$	CH_2Cl_2	−40	14.7	1.66	0.3	18
$P\dot{h}$	Benzene	+20	12.3	$a^H_o = a^H_p = 2.0$	$a^H_m = 0.9$	33
$Ph\dot{C}H_2$	Toluene	+20	14.2	7.5	—	30, 33
$CH_3\dot{O}$	Methanol	−80	29.5	1.54	—	11, 35, 12
$C_2H_5\dot{O}$	Ethanol	−80	29.1	1.1	—	11, 12
n-$C_3H_7\dot{O}$	1-Propanol	−80	29.4	1.2	—	11
iso-$C_3H_7\dot{O}$	2-Propanol	−80	29.4	—	—	11
t-$Bu\dot{O}$	Benzene	+20	26.6	—	—	33
$\dot{C}H_2OH$	Methanol	−80	14.4	4.0	—	11, 35
$\dot{C}H_2OH$	Methanol	+20	14.2	4.8	—	33
$CH_3\dot{C}HOH$	Ethanol	−80	14.5	2.0	—	11
$C_2H_5\dot{C}HOH$	1-Propanol	+20	14.1	1.8	—	33
R—$\dot{C}O$	Benzene	−20	8.0	—	—	34
H—$\dot{C}O$	$CHBr_3$	−20	7.0	1.4	—	25, 38
$CH_3\dot{S}$	CH_3SH	−103	18.9	1.2	—	36
$C_3H_7\dot{S}$	C_3H_7-SH	−85	17.8	—	—	36
$Ph\dot{C}HCHO$	Benzene	+40	14.6	3.7	1.3	39
$CH_3CO\dot{C}H_2$	Acetone	120	14.8	8.3	—	31
$CH_3\dot{C}HCOCH_3$	Ketone	+20	14.6	2.5	—	31
$\dot{C}H_2COOH$	Water	+20	16.1	8.4	—	37
$PhCO\dot{C}H_2$	$PhCOCH_3$	+25	14.4	7.9	—	31
$HOC(CH_3)_2\dot{C}H_2$	t-Butyl alcohol	+30	15.4	11.0	—	40
$Et_2N\dot{C}HCH_3$	Et_3N	+20	14.3	4.06	—	39
t-Bu	Methanol	+20	16.0	—	—	18, 32
$\dot{C}F_3$	CH_2Cl_2	−60	12.2	$a_F = 12.5$	—	31
$\dot{C}Cl_3$	$CHCl_3$	+20	12.5	$a_{Cl} = 2.2$	—	33
$\dot{O}H$	Water	+20	28.0	$a^H_{OH} = 4.4$	—	66

The interpretation of data on the trapping of TNB radicals in the presence of oxidants and in electron-donating media must therefore be approached with caution.

2-Methyl-2-nitroso-3-butanone is similar to TNB as regards its chemical properties and the EPR spectra of radical adducts[2,18] and is sometimes a more effective radical acceptor. When this compound is acted upon by ultraviolet light, acyl radicals are formed and then trapped.

Fully fluorinated t-nitrosobutane is also used to trap unstable radicals[21,22].

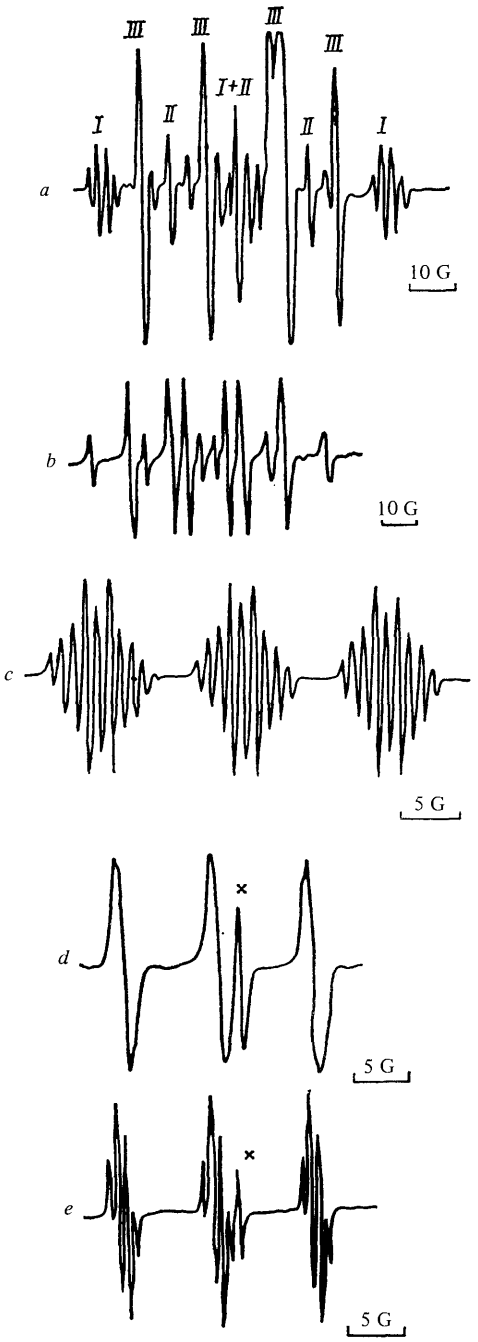
The EPR spectra of the radical adducts of TNB and 2-methyl-2-nitroso-3-butanone have a triplet due to splitting by the nitrogen atom of the nitroso-group and additional hyperfine structure arising as a result of the interaction with the magnetic nuclei of the trapped radical. Splitting by the t-butyl group is not observed. The trapped radical can be identified on the basis of the nature of the additional hyperfine structure, the constants for splitting by nitrogen atoms (a_N) or β-hydrogen (a^H_β), and in certain cases γ-hydrogen (or heteroatoms). Table 2 presents the splitting constants for the most characteristic TNB radical adducts. The values of a_N are different for different classes of organic radicals: a_N = 26–29 G for RO· radicals, 14–16 G for alkyl radicals, and 7–8 G for acyl radicals. Definite regularities in the variation of the constants for splitting by hydrogen and heteroatoms, associated with the structure of the trapped radical, have been observed. In polar solvents, the splitting constants can increase by 1–2 G relative to non-polar solvents and comparative measurements must therefore be performed in identical solvents. One must note that, owing to the broadening of the EPR lines due to the influence of the t-butyl group, a splitting smaller than 0.3 G is not resolved in the spectra.

An appreciable improvement of the resolution of the EPR spectra can be achieved by employing fully deuterated t-nitrosobutane $(CD_3)_3CNO$, whose synthesis has already been described[24]. The adducts of this trapping agent give rise to very narrow lines in EPR spectra, which makes it possible to observe additional splitting due to γ-protons or radicals with heteroatoms, which cannot be resolved in the case of the usual TNB. In addition, the signal to noise ratio is improved[23–26]. For example, splitting by the protons of the CH_3 group due to the hyperfine (HF) interaction via the carboxy-group has been observed for the adduct of $(CD_3)_3CNO$ with the radical $CH_3O\dot{C}O$ (Figs. *d* and *e*)

2. AROMATIC NITROSO-COMPOUNDS

(a) Nitrosobenzene

The disadvantages of TNB described above (sensitivity to light, oxidants, strong acids, and certain anions as well as instability of many adducts) limit the application of this trapping agent. Nitrosobenzene has some advantages compared with TNB[19]. It is readily available, exists in solution largely in the active monomeric form, and is not sensitive to light at wavelengths in excess of 360 nm. Only ultraviolet light with $\lambda < 310$ nm leads to the formation of the diphenylnitroxy-radical. Spin adducts with nitrosobenzene are usually stable at 20°C and their EPR spectra contain very narrow lines, so that very small splittings are resolved in the latter. The main disadvantage of nitrosobenzene is difficulty of analysing its EPR spectra, because addition HFS lines due to the benzene ring protons arise ($a^H_o = a_p = 2.5$ G, $a^H_m = 0.9$ G). The spectra simplify when 3,5-dideuteronitrosobenzene is used instead of nitrosobenzene, but the replacement itself leads to a broadening of the lines due to an unresolved HFS caused



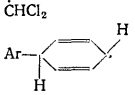
EPR spectra of the adducts of t-nitrosobutane (TNB) with trapped radicals: *a*) irradiation of methanol with electrons having an energy of 3 MeV at −45°C directly in the resonator[30] [I) $CH_3O-N(\dot{O})-t\text{-}Bu$: II) $HOCH_2-N(\dot{O})-Bu\text{-}t$; III) $H-N(\dot{O})-Bu\text{-}t$]; *b*) adducts of TNB with the $\dot{C}H_3$ radical in benzene, obtained on decomposition of acetyl peroxide[15,33]; *c*) adduct of TNB with the phenyl radical in benzene at 20°C (thermal decomposition of benzoyl peroxide)[147]; *d*) adduct of TNB with the $CH_3O\dot{C}O$ radical; *e*) adduct of perdeutero-t-nitrosobutane with the $CH_3O\dot{C}O$ radical (in contrast to case *d*, the lines due to the CH_3 group are evidently resolved); the cross denotes one of the lines due to the adduct with the t-BuO· radical.

by the influence of the deuterium nuclei[19]. Substituted nitrosobenzene derivatives, which are free from the disadvantages of nitrosobenzene, have been used as spin-trapping agents[41-43].

(b) Nitrosodurene (2,3,5,6-tetramethylnitrosobenzene)[41]

Nitrosodurene (ND), synthesised by the method of Smith and Taylor[44], is a colourless dimer in the crystalline state; even in solutions it exists largely in the dimeric form. On heating, the degree of dissociation of the dimer increases and a greenish colour appears. Nitrosodurene is appreciably soluble in $CHCl_3$ and methylene chloride; in aromatic hydrocarbons its solubility is about 0.003 M and in other solvents it is even smaller. However, in consequence of the high trapping rate constants, such nitrosodurene concentrations are sufficient to trap short-lived radicals. The main advantages of nitrosodurene as a spin-trapping agent are simplicity of the EPR spectra of its spin adducts and the large amount of information contained in them, insensitivity to ultraviolet light, and high stability of radical adducts at 20°C. The EPR spectra exhibit hyperfine splitting by the nitrogen atom of the NO group and by the protons of the trapped radical.

Table 3. Parameters of the EPR spectra of the adducts formed as a result of the capture of radicals by nitrosodurene in benzene at 20°C.[41]

Radical	*g*-Factor	a_N, G	a_β^H, G	Splitting by other atoms
$\dot{C}H_3$	2.0060	13.7	12.17	
$\dot{C}H_3$	2.0061	14.4	13.6	(t-Butyl alcohol (Ref.40))
$\dot{C}_2H_5$	2.0061	13.68	10.97	—
$PhCH_2\dot{C}H_2$	2.0060	13.59	10.87	—
$CH_2{=}CH{=}\dot{C}H_2$	2.0060	13.57	10.20	—
$Ph\dot{C}H_2$	2.0061	13.61	7.93	—
$PhO\dot{C}H_2$	2.0062	12.00	4.84	—
Ph·	2.0057	10.11	$a_o^H=a_p^H=2.78$ $a_m^H=0.95$	—
$\dot{C}_6H_4OH$-*p*	2.0050	11.80	$a_o^H=3.25$; 2.75 $a_m^H=a_m^H=0.83$	—
$\dot{C}H_2OH$	2.0059	13.91	7.71	—
$C_2H_5\dot{C}HOH$	2.0060	13.75	3.39	—
t-BuO	2.0054	25.18	—	—
t-Bu·	2.0061	13.6	—	—
$\dot{C}Cl_3$	2.0071	10.73	—	$a_{Cl}=1.31$
$\dot{C}HCl_2$	2.0068	11.13	1.14	$a_{Cl}=3.01$
	—	13.5	8—14	161

The splitting by the *para*-protons and the protons of the CH_3 groups is not resolved, but the lines are broadened owing to the interaction with these protons. The HFS lines of the radical adducts of deuterated nitrosodurene [2,3,5,6-tetrakis(trideuteromethyl)nitrosobenzene] are appreciably narrowed, but splitting by the *para*-protons is manifested (a = 0.34 G).[41] The parameters of the EPR spectra of the nitrosodurene adducts are presented in Table 3. All alkyl radicals, including tertiary radicals, add to nitrosodurene via the nitrogen atom and do not form anilino-radicals. The presence of electronegative groups reduces a_N and increases the g-factors. The values of

a_{β}^{H} depend greatly on the structure of the trapped radical. The disadvantages of nitrosodurene include poor solubility in many compounds, the broadening of the lines, and lability of adducts with RO· radicals.

(c) 2,4,6-tri-t-butylnitrosobenzene (BNB)[42,43,45]

Compared with other spin-trapping agents, BNB has a number of advantages. 1. It dissolves readily in many solvents and exists in the active monomeric form in both the solid state and in solution. 2. The spin adducts of BNB have simple, satisfactorily resolved EPR spectra, but the latter show splitting due to *meta*-protons. 3. BNB is a bifunctional trapping agent: radicals can add both to the nitrogen atom, forming nitroxy-radicals, and to the oxygen atom of the nitroso-group with formation of *N*-alkoxy-anilino-radicals (the reaction pathway is determined by the structure of the precursor radical):

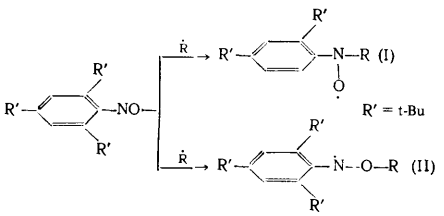


Table 4. Parameters of the EPR spectra of the radical adducts of 2,4,6-tri-t-butylnitrosobenzene.

Radical	Type of adduct	Solvent	*g*-Factor	a_N, G	a_{β}^{H}, G	a_m^H, G	Splitting by other atoms
H·	I	Benzene	2.0061	11.65	—	1.03	12.96 (α-H)
H·	I	Methanol	2.0062	12.7	—	0.9	15.0 (α-H)
ĊH$_3$	I	Benzene	2.0060	13.03	12.33	0.81	—
ĊH$_3$	I	*t*-Butyl alcohol	2.0061	14.2	13.4	0.9	—
Ċ$_2$H$_5$	I	Benzene	2.0060	13.46	17.99	0.83	—
n-Ċ$_4$H$_9$	I	Benzene	2.0061	13.44	17.97	0.78	—
(CH$_3$)$_2$CHĊH$_2$	I	Benzene	2.0061	13.57	18.27	0.84	—
(CH$_3$)$_2$ĊH	I	Benzene	2.0061	13.29	22.19	0.76	0.38 (6-γ-H)
C$_2$H$_5$(CH$_3$)ĊH	I	Benzene	2.0061	13.33	22.25	0.76	0.39 (5-γ-H)
CH$_2$=CH—ĊH$_2$	I	Benzene	2.0060	13.40	16.42	0.84	—
Ph·	I	Benzene	2.0057	9.88	—	0.63	2.86 (2-*o*-H) 2.61 (1-*p*-H) 0.92 (2-*m*)-H
PhĊH$_2$	I	Benzene	2.0061	13.62	14.75	0.83	—
ĊH$_2$OH	I	Methanol	2.0062	13.9	13.9	1.0	—
CH$_3$ĊHOH	I	Ethanol	2.0060	12.60	14.4	0.96	0.12 (12H)
CH$_3$O·	I	Methanol	2.0054	24.0	2.0	0.9	—
C$_2$H$_5$Ȯ	I	Ethanol	2.0052	24.0	2.7	0.9	—
ĊH$_2$(CH$_3$)$_2$COH	II	t-Butyl alcohol	2.0040	11.7	—	2.1	2.1 (2-R-H)
(CH$_3$)$_2$ĊH	II	Benzene	2.0040	11.01	—	1.82	1.82 (1-R-H)
Ċ$_6$H$_{11}$	II	Cyclohexane	2.0040	10.95	—	1.79	1.79 (1-R-H)
t-Bu·	II	Benzene	2.0040	10.26	—	1.90	—
Si(C$_2$H$_5$)$_3$	II	Benzene	2.0040	10.33	—	1.96	—
CH$_3$COĊH$_2$	I	Acetone	2.0060	13.47	14.93	0.82	—
PhOĊH$_2$	I	Anisole	2.0064	12.23	9.85	0.82	—

*Here I = nitroxy-radical and II = anilino-radical.

The EPR spectra of *N*-alkoxyanilino-radicals can be readily distinguished from the spectra of nitroxy-radicals, because their *g*-factor and the constant for splitting by the nitrogen atom (Table 4) are smaller and the line width is greater than for nitroxy-radicals. 4. The majority of BNB adducts are stable in non-polar solvents at 20°C. 5. BNB is not photolysed in solution, which makes it possible to use it in the study of photochemical reactions.

Primary alkyl radicals react with BNB, forming exclusively nitroxy-radicals. Tertiary alkyl radicals add only to the O atom with formation of anilino-radicals. Secondary alkyl radicals add to both N and O atoms. Like tertiary alkyl radicals, triethylsilyl and triethylstannyl add to the oxygen atom. Certain radicals with heteroatoms (t-BuO·, the phenoxy-radical, ĊCl$_3$, the *N*-methylanilino-radical, Ṡ–Ph, etc.) are either ineffectively trapped or do not form stable adducts with BNB. However, BNB is perhaps the best spin-trapping agent for alkyl radicals, since the EPR spectra of their spin adducts are the most sensitive to changes in the structure of the radicals. Among other substituted nitrosobenzenes, the following compounds may be noted.

2,4,6-Trimethoxycarbonylnitrosobenzene[41] is a colourless dimer in the solid state, but dissociates almost completely in solution. In terms of the nature of the spin adducts, this nitroso-compound resembles nitrosodurene, but is a more convenient spin-trapping agent because of its high solubility and the very small width of the lines due to the spin adducts.

2,4,6-Trimethoxynitrosobenzene[41] has properties similar to those of nitrosodurene and the spectra of the spin adducts are simple and have narrow HFS lines. The compound itself is resistant to photolysis but is poorly soluble in many solvents.

2,4,6-Trichloronitrosobenzene[41] largely dissociates in solution but is not photolysed.

Pentafluoronitrosobenzene[41] is a monomer even in the crystalline state, is not photolysed in solution, but has been little investigated as a spin-trapping agent.

3. NITRONES

When the radicals Ṙ are trapped by nitrones having the general formula R′–CH=N(O)–R″, the products are the nitroxy-radicals R′–$\underset{\text{R}}{\text{CH}}$–$\underset{\text{O}}{\text{N}}$–R″, whose EPR spectra consist in most cases of a triplet of doublets (splitting by the nitrogen atoms and β-hydrogen atoms). The HFS due to the trapped radicals is usually not resolved and special mention shall be made of the exceptions to this rule. Nitrones can be used conveniently as spin-trapping agents, because of their high reactivity, ready solubility in many compounds, the simplicity of their EPR spectra, and the stability of the spin adducts.

(a) *C*-Phenyl-*N*-t-butylnitrone (PBN)

The majority of workers have synthesised PBN by Emmons' method[46]. The spectrum of PBN in solution in ethanol has an absorption band with a maximum at 294 nm (ϵ_{294} = 16 700 litre mole^{-1} s^{-1}) at 20°C.[46] The compound is stable and relatively insensitive to light, O_2, and water vapour, and dissolves readily in the majority of solvents (its solubility ranges from 0.1 to 1.0 M). Many adducts with PBN are stable at room temperature. In a highly acidic medium PBN hydrolyses with formation of hydroxylamine and benzaldehyde[46]. In the presence of oxidants [Cl_2, Br_2, NO_2, nitrosyl chloride, t-butyl nitrite, $KMnO_4$, and $Pb(AcO)_4$] the stable benzoyl-t-butylnitroxy-radical is formed[47–50] (triplet with a_N = 7.5–8 G).

The data concerning the resistance of PBN to ultraviolet light are contradictory. After prolonged photolysis of solid PBN, the formation of an unidentified radical (triplet in EPR spectra with a_N = 15.2 G) was noted[51]. However, radicals were not detected after ultraviolet irradiation of PBN solutions in methanol, ethanol, and benzene. On the other hand, photolysis of methanol in the presence of PBN led to the observation of the EPR spectrum of an adduct with $\dot{C}H_2OH$ radicals, while irradiation through a filter containing 0.5 M PBN does not lead to the appearance of radicals[55]. It is believed that the photoexcited PBN molecule is capable of abstracting a hydrogen atom from the solvent molecule.

The formation of the radical Ph–C(O)–N(Ȯ)–Bu-t was observed after intense ultraviolet irradiation of PBN solutions in benzene. A possible mechanism of the formation of this radical is based on the intermediate formation of the oxazirane Ph–C(O)(H)–N–Bu-t.[52,53] The contradictory nature of the data of different workers on the photochemical stability of PBN can be attributed not only to the complexity of the processes taking place but also to the purity of the reagent as well as the presence of oxygen in solution. It is noteworthy that no stable radicals are formed during the preparation of PBN solutions in daylight in alcohols and hydrocarbons.

Like other nitrones, PBN is an effective trapping agent not only for radicals but also for certain anions (nitromethane, phthalimide, benzyl cyanide, and styrene anions), the trapping process resulting in the formation of the corresponding nitroxy-radicals. The presence of traces of air increases the yield of these radicals[20,56]. Nitrones readily enter into the 1,3-dipolar addition reaction, which limits their use as spin-trapping agents. Examples of this are provided by the addition of HCN[20] and acetates[47]. At 20°C in the absence of light both $Pb(AcO)_4$ in benzene solution and CH_3COOK in acetic acid[20,47] react with PBN to form a spin adduct (a_N = 12.8 G, a_β^H = 1.73 G) indistinguishable from the adducts of PBN with the radical $CH_3C\dot{O}O$:

$$Ph{-}CH{=}\overset{+}{N}{-}Bu\text{-}t + Pb(OAc)_4 \rightarrow Ph{-}CH(O^-){-}N{-}Bu\text{-}t$$

$$\rightarrow Ph{-}CH(AcO){-}N(OPb(OAc)_3){-}Bu\text{-}t \xrightarrow{em} Ph{-}CH(AcO){-}N(O\cdot){-}Bu\text{-}t .$$

Slow oxidation of this adduct with air leads to the appearance of the benzoyl-t-butylnitroxy-radical.

Caution is necessary in the interpretation of the mechanism of the formation of the spin adducts of PBN with the radicals $CH_3C\dot{O}O$ and $PhC\dot{O}O$, arising in the thermal decomposition of acetates and benzoates, since the same spin adducts can appear also in the nucleophilic addition of acetate and benzoate ions to PBN[20,49].

PBN reacts readily with Grignard reagents and organometallic compounds of sodium, potassium, etc., the process being accompanied by the intermediate formation of the hydroxyamide anion, which oxidises in air to the corresponding nitroxy-radical[47,56]:

$$LiR + PhCH{=}N(O){-}Bu\text{-}t \rightarrow Ph{-}CH(R){-}N(OLi){-}Bu\text{-}t \xrightarrow{O_2} Ph{-}CH(R){-}N(O\cdot){-}Bu\text{-}t .$$

This property of nitrones is used for the "specific synthesis" of nitroxy-radicals in order to identify them.

The EPR spectra of the PBN radical adducts Ph–CHR–N(O·)–Bu-t consist of a triplet of doublets (as a result of splitting by the nitrogen atom and the β-proton) with small differences in the splitting constants a_N and a_β^H. As stated above, splitting by the nuclei of the trapped radical $\dot{R}$ is not manifested with the exception of adducts with H atoms and inorganic radicals (Table 5). In order to identify the trapped radicals, a very accurate (to within 0.03G) measurement of the hyperfine splitting constants is necessary (for comparison with the available literature data). The solvent has an appreciable influence on the splitting constants: they increase in more polar systems. The "specific synthesis" of nitroxy-radicals in the same solvent is necessary for identification in many instances. The measurement of the width of the line due to adducts may be of some assistance in identification. For example, the adducts of PBN with the radicals $CH_3\dot{O}$ and $\dot{C}H_2OH$ have lines with widths of 0.5 and 1.2 G respectively[57,58]. This difference is associated with the unresolved HFS due to the protons of the $\dot{C}H_2OH$ radical. Thus the EPR spectra of PBN adducts with trapped radicals contain much less information about the nature of the trapped radicals than in the case of nitroso-compounds.

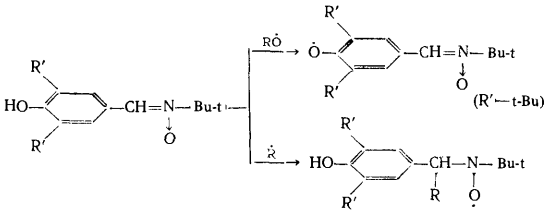
Table 5. Parameters of the EPR spectra of the radical adducts of *C*-phenyl-*N*-t-butylnitrone (PBN).

Radical	Solvent	*T*, °C	a_N, G	a_β^H, G	Splitting by other atoms	Refs.
Ḣ	Benzene	+25	14.8	7.4	—	61
Ḣ	Alcohols	−30	15.8	8.3	—	57, 58
$\dot{C}H_3$	Benzene	+25	14.2	3.45	—	47
$\dot{C}_2H_5$	Benzene	+25	13.9	3.2	—	47
Ṗh	Benzene	+25	13.8	2.1	—	47, 67
Ṗh	Alcohols	+25	15.25	3.14	—	136
$Ph\dot{C}H_2$	Toluene	120	13.9	2.3—2.45	—	47
$\dot{C}H_2OH$	Methanol	+20, +30	15.5	3.75	—	57—59
$CH_3\dot{C}HOH$	Ethanol	+20	15.44	3.6	—	57—59
$CH_3\dot{O}$	Methanol	+20, −30	14.5	2.8	—	57—59
$C_2H_5\dot{O}$	Ethanol	+20	14.49	2.67	—	59
$(CH_3)_2CH\dot{O}$	2-Propanol	+20	14.52	2.18	—	59
$(CH_3)_2\dot{C}OH$	2-Propanol	+20	15.36	3.59	—	59
F·	Benzene	+25	12.2	1.18	a (F)=45.6	1
Cl·	Benzene	+25	12.1	0.75	6.05 (^{35}Cl); 4.88 (^{37}Cl)	1
$CH_3C\dot{O}O$	Benzene	+20	12.8—13.03	1.73—1.92	—	47
$PhC\dot{O}O$	Benzene	+20	12.6—12.85	1.29—1.48	—	46
$\dot{C}N$	Benzene	+20	14.4	5.5	a_γ^N=1.2	160
$\dot{C}H_2CN$	Acetonitrile	+20	14.9	3.9	a_γ^H=0.65	160
$\dot{C}H_2CN$	Benzene	+20	14.7	3.7	a_γ^H=0.6	160
$\dot{C}H(CN)_2$	$CH_2(CN)_2$	+20	14.8	5.0	a_γ^H=0.68	160
$\dot{C}H(CN)_2$	Benzene	+20	14.5	3.9	a_γ^H=0.65	160

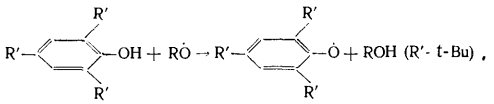
(b) Bifunctional Trapping Agents

Among other nitrones, the attention of investigators has been drawn to bifunctional trapping agents. α-(3,5-Di-t-butyl-4-hydroxyphenyl)-N-t-butyl-nitrone has been described[62]. Oxygen-containing radicals ($R\dot{O}$, $Ac\dot{O}$, $PhC\dot{O}O$, etc.) react with the nitrone by abstracting the phenolic hydrogen with formation of stable phenoxy-radicals; the solution is then coloured blue. Radicals with the unpaired electron at a carbon atom add to the β-carbon

atom of the nitrone, forming nitroxy-radicals, which colour the solution yellow-orange. The EPR spectrum of the phenoxy-radical (a_N = 5.05 G, a_β^H = 2.1 G, a_m^H = 1.7 G) differs strongly from the spectrum of the nitroxy-radical (a_N = 13.5–15.5 G, a_β^H = 2.3–4.2 G). The formation of oxygen-containing radicals in the system can be readily established on the basis of EPR and optical absorption spectra[62]:

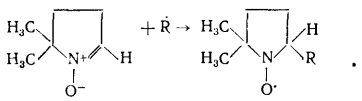


Together with this nitrone, an equimolar mixture of more readily available substances, PBN and 2,4,6-tri-t-butylphenol, can be used with equal success as a bifunctional trapping agent[63]. The PBN and phenol concentrations can be varied, the EPR spectral line of the phenoxy-radical formed is narrower than in the case of the preceding trapping agent, and the satellites due to the 13C atom of the phenoxy-radical are not superimposed on the weaker lines of the nitroxy-radicals:



(c) Cyclic Nitrones

The addition of short-lived radicals to five-membered nitrones of the pyrrolidine series has been studied[64–68]. Among them, 5,5-dimethylpyrroline 1-oxide (DMPO) is of greatest interest[64–68]:

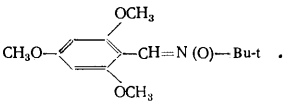


All radicals with the unpaired electron localised mainly at a carbon atom react with DMPO to form adducts whose EPR spectra consist of a triplet of doublets but the splittings by the β-proton are significantly greater than by nitrogen (in contrast to PBN). For adducts with hydroxyalkyl radicals (with the exception of $\dot{C}H_2OH$), the splitting by β-protons is greater by 2–3 G than in the case of alkyl radicals, while for adducts with acyl, benzoyl, and $\dot{C}F_3$ radicals, it is smaller by several gauss.

In the EPR spectra of DMPO adducts with oxy-radicals (RȮ, AcȮ, BzȮ, etc.) there is additional splitting due to one of the γ-protons and the splitting by β-protons is smaller almost by a factor of 3 than for adducts with alkyl radicals (Table 6). The EPR lines of the adducts with RȮ radicals can therefore be readily distinguished from the spectra of other adducts.

The spin adducts of DMPO are stable at 20°C, have narrow lines in the EPR spectra, and the trapping agent itself exhibits a high efficiency in the trapping of radicals (Table 7) and can be conveniently used to trap oxy-radicals.

N-(2,3,5,6-Tetramethylphenyl)nitrone and methyl-*N*-(2,3,5,6-tetramethylphenyl)nitrone[41] as well as 2,4,6-trimethoxy-PBN[156] have been proposed for the trapping of oxy-radicals:



The adducts of these nitrones with oxy-radicals are stable and have EPR parameters which differ markedly from those of other radicals.

Table 6. Parameters of the EPR spectra of the radical adducts of DMPO[64–68].

Radical	Solvent	a_N, G	a_β^H, G	a_γ^H, G	Refs.
Ḣ	Water	16.7	22.4	—	66
ȮH	Water	15.0	15.0	—	66
$\dot{C}H_3$	Benzene	14.3	20.52	—	64
n-$\dot{C}_4H_9$	Benzene	14.24	20.41	—	64
$Ph\dot{C}H_2$	Benzene	14.16	20.66	—	64
Pḧ	Benzene	13.76	19.22	—	64
$\dot{C}H_2OH$	Benzene	14.66	20.67	—	64
$CH_3\dot{C}HOH$	Benzene	15.03	22.53	—	64
$(CH_3)_2\dot{C}OH$	Benzene	14.58	23.91	—	64
$CH_3\dot{C}{=}O$	Benzene	14.03	17.87	—	64
$Ph\dot{C}{=}O$	Benzene	13.99	15.57	—	64
$NH_2\dot{C}{=}O$	Benzene	15.23	18.56	—	64
$\dot{C}F_3$	Benzene	13.22	15.54	1.01 (3-F)	64
$CH_3\dot{O}$	Benzene	13.58	7.62	1.85 (1-H)	64
$C_2H_5\dot{O}$	Benzene	13.11	7.93	1.97 (1-H)	64
t-BuȮ	Benzene	12.24	9.63	0.87 (2-H)	64

Table 7. The rate constants for the trapping of radicals by spin-trapping agents.

Radical	Spin-trapping agent	Matrix	T, °C	k, litre mole^{-1} s^{-1}	Refs.
t-BuȮ	t-BuNO	Benzene	+25	$1.6\cdot10^8$	68
t-Bu̇	CH_2 = N(O)-Bu-t	Benzene	+25	$3.5\cdot10^8$	68
t-Bu̇	PBN	Benzene	+25	$5.5\cdot10^8$	68
t-Bu̇	p-NO_2-PBN	Benzene	+25	$9.0\cdot10^8$	68
t-Bu̇	p-Cl-PBN	Benzene	+25	$6.5\cdot10^8$	68
t-Bu̇	p-CH_3-PBN	Benzene	+25	$3.4\cdot10^8$	68
t-Bu̇	p-CH_3O-PBN	Benzene	+25	$5.5\cdot10^8$	68
t-Bu̇	DMPO	Benzene	+25	$5.0\cdot10^8$	68
$\dot{C}F_3$	CF_3NO	Benzene	+25	$5.8\cdot10^7$	68
t-BuOC̈O	TNB	Benzene	+40	$1.1\cdot10^8$	95
Pḧ	PBN	Benzene + alcohol	+20	$1.2\cdot10^7$	135
PhCOȮ	PBN	Benzene + alcohol	+20	$4.0\cdot10^7$	135
$CH_3\dot{O}$	PBN	Methanol	+20	$1.2\cdot10^8$	58
$CH_3\dot{O}$	TNB	Methanol	−45	$1.3\cdot10^8$	157
$C_2H_5\dot{O}$	PBN	Ethanol	+20	$2.0\cdot10^8$	139

(d) t-Butylmethylenenitrone

t-Butylmethylenenitrone (MN) CH_2=N(O)=Bu-t has been proposed[33,69] as a spin-trapping agent and its application in radiation chemistry has been described[40,70]: MN is synthesised by the reaction of TNB with diazomethane[71,72].

This nitrone is readily soluble in water, alcohols, and many organic solvents. It is not photolysed by light with a wavelength in excess of 300 nm, but light with shorter wavelengths leads to the formation of the radical t-Bu–CH_2–N(Ȯ)–Bu-t (a_N = 13.1 G, a^H_β = 7.0 G). The splitting by β-protons in the spectra of radical adducts of MN depends greatly on the nature of the trapped radical and there is also splitting by the nuclei of the added radical $\dot{R}$. The EPR spectra of the adduct of MN with the radical $\dot{R}$ have the same parameters as the spectra of the adducts of TNB with the radicals $R\dot{C}H_2$ (where R is an H atom or a radical group):

$$\dot{H} + CH_2{=}N(O){-}Bu\text{-}t \rightarrow CH_3{-}N(\dot{O}){-}Bu\text{-}t \leftarrow t\text{-}BuNO + \dot{C}H_3 ,$$
$$\dot{C}_6H_5 + CH_2{=}N(O){-}Bu\text{-}t \rightarrow C_6H_5CH_2{-}N(\dot{O}){-}Bu\text{-}t \leftarrow t\text{-}BuNO + C_6H_5\dot{C}H_2 .$$

4. OTHER SPIN-TRAPPING AGENTS

Apart from nitroso-compounds and nitrones, organic compounds of other classes have been used as spin-trapping agents (Table 1). The *N*-oxides of aromatic nitriles trap unstable radicals, forming fairly stable iminoxy-radicals[73], and no less information is obtained about the structure of the trapped radical than in the case where nitroso-compounds are used:

$$Ar{-}C{\equiv}N{\rightarrow}O + \dot{R} \rightarrow \begin{matrix} Ar \\ R \end{matrix}\!\!>\!C{=}N{-}\dot{O} .$$

For example, the spectra of adducts with the radicals $R{-}\dot{C}O$ show splitting by the group R.[73] A deficiency of these trapping agents is that the geometrical isomers of the same iminoxy-radical have different EPR spectra, which complicates analysis.

The formation of adducts of certain organophosphorus compounds with radicals t-BuȮ has been observed.[80] The formation of radicals of this type can be of interest for organophosphorus chemistry:

$$t\text{-}Bu\dot{O} + (C_6H_5O)_2PCl \rightarrow (C_6H_5O)_2\dot{P}Cl(O{-}Bu\text{-}t) .$$

Substituted acetylenes[81] (for example, $CF_3{-}C{\equiv}C{-}CF_3$, $C_6H_5{-}C{\equiv}C{-}C_6H_5$) can be used as spin-trapping agents. The trapping process involves the formation of 1,2-disubstituted or trisubstituted vinyl radicals, the lifetimes of certain radicals at 20°C exceeding 1 h.

The ability to trap unstable radicals with formation of stable radical adducts is also possessed by perfluoroketones $(CF_3)_2CF{-}\underset{\underset{O}{|}}{C}{-}CF(CF_3)_2$[82] and di-t-butyl selenoketone[151].

5. SPIN-TRAPPING AGENTS IN AQUEOUS SOLUTIONS

Poor solubility frequently limits the application of spin-trapping agents in aqueous solutions. For example, DMPO, PBN, and TNB dissolved in water to an extent less than 0.1 M.[66] An exception is MN, which readily dissolves in water (see above).

In order to investigate the radicals arising in aqueous solutions, maleate and fumarate anions[74] as well as the amides and imides of maleic acid have been used[75]. These trapping agents can be employed particularly to trap ȮH radicals and H atoms.

Many inorganic and aromatic radicals arising in the radiolysis of aqueous solutions and in the reactions of ȮH radicals and $SO_4^{\dot{-}}$ radical-ions (generated, for example, in the photolysis of H_2O_2 and persulphate) with inorganic anions and aromatic compounds[83-86] have been identified[76-79] with the aid of nitromethane in the *aci*-form $CH_2{=}NO_2^-$ in an alkaline medium. Two types of reaction take place with the nitromethane anion: the addition of the inorganic radical $\dot{X}$ to the C=N bond with formation of the adduct $X\dot{C}H_2\dot{N}O_2^-$ and electron transfer from $CH_2{=}NO_2^-$ to the inorganic anion with formation of $\dot{C}H_2NO_2$, which also adds to the nitromethane anion. The constants for hyperfine splitting by the nitrogen atom and methylene protons in the radical-anion $X\dot{C}H_2\dot{N}O_2^-$ depend greatly on the nature of the trapped radicals; splitting due to the trapped radicals sometimes appears in the spectrum (X = CN, HPO_2^-).

The radical adducts with the nitromethane anion have short lifetimes (less than a second) and their detection requires the continual generation of radicals in the resonator (under an electron beam or with the aid of a flow technique). Direct detection of the majority of inorganic radicals in aqueous solution under an electron beam (without spin-trapping agents) is impossible[86], because the radicals themselves have shorter lifetimes by several orders of magnitude.

6. STABILITY OF RADICAL ADDUCTS AND THEIR SECONDARY REACTIONS

The stability of nitroxy-radicals is determined by the possibility of tautomeric transformations[7,8], the type of substituent at the nitrogen atom, temperature, and the solvent. Certain nitroxy-radicals can react with one another to form diamagnetic compounds[87-89]. It has been shown in the study of the reactions of dialkyl- and diaryl-nitroxy-radicals that the rate constants for the destruction of these radicals depend on the nature of the solvent[87]. For example, in isopentane the rate constant for the destruction of nitroxy-radicals is 40 times greater than in water. The formation of hydrogen bonds and complexes of nitroxy-radicals with a polar solvent is well known[8]. The solvation of the radical centre as well as other groups (for example, OH groups) alters the reactivity of the radical. For example, the adducts of TNB and PBN with the radicals RȮ are appreciably less stable than the adducts with the radicals $R\dot{C}HOH$.[12,57,58] The increased stability of the adducts of $R\dot{C}HOH$ has been explained by the formation of a hydrogen bond with the solvent and also an intramolecular hydrogen bond[12,58,70].

The PBN adducts are much more stable than the TNB adducts with the analogous radicals, which is due to the stabilising influence of the phenyl groups. For example, the adducts of TNB with alkyl radicals can be observed in the liquid phase either at a low temperature or under the conditions of continuous generation of radicals[18,27,32,33,90], while the analogous adducts with PBN are observed under steady-state conditions at 20°C (including the adduct with H atoms)[57,58,91,92].

In order to avoid an error in the interpretation of the mechanisms of the formation of radicals, account must be taken of the possibility of rapid secondary reactions of spin adducts with one another and with the spin-trapping agent. For example, the adduct of TNB with the radical $\dot{C}Cl_3$ is transformed as a result of secondary reactions into an adduct of TNB with the radical $Cl\dot{C}O$.[38] The absence of an adduct of TNB with the radical $\dot{C}H_2OH$ in γ-irradiated methanol has been explained[35] by the fact that $\dot{C}H_2OH$ is a secondary radical and appears in the reaction of $CH_3\dot{O}$ with methanol. The use of another trapping agent (PBN) showed that in radiolysis both radicals are primary species[57,58,92].

Nitroxy-radicals with a mobile β-hydrogen atom disproportionate with formation of hydroxylamine and a nitrone[87,88,93]:

$$2\left(\text{—CH}_2\text{—N—R}\right) \rightarrow \text{—CH=N—R} + \text{—CH}_2\text{—N—R}$$

(O· on the left; O on the nitrone; OH on the hydroxylamine)

The reaction between the adducts of TNB with H atoms and the radicals $\dot{C}H_2OH$ proceeds via the same mechanisms[12]:

$$\text{t-BuN(}\dot{\text{O}}\text{)H} + \text{HOCH}_2\text{—N(}\dot{\text{O}}\text{)—Bu-t} \rightarrow$$
$$\rightarrow \text{t-BuN(OH)H} + \text{HOCH=N(O)—Bu-t}\ .$$

Both radical adducts are detected with the aid of EPR spectra only under an electron beam and rapidly disappear after the beam is switched off, although the TNB adduct with the $\dot{C}H_2OH$ radical is itself stable at 20°C.[12,94]

The adduct of TNB with the radicals t-Bu$\dot{O}$ decomposes (the decomposition rate constant in benzene[95] at 40°C is 1.1×10^{-3} s^{-1}) with formation of the radicals t-$\dot{B}$u, which add to the TNB molecule, forming the stable radical t-$Bu_2N\dot{O}$:[95]

$$\text{t-BuON(}\dot{\text{O}}\text{)—Bu-t} \rightarrow \text{t-BuNO}_2 + \text{t-}\dot{\text{B}}\text{u} \xrightarrow{\text{t-BuNO}} \text{t-Bu}_2\text{N}\dot{\text{O}}\ .$$

The adducts of t-Bu$\dot{O}$ radicals with nitrosodurene[40] and probably with other trapping agents decompose analogously.

The nitroxy-radicals arising in the trapping of unstable radicals by nitrones and nitroso-compounds can trap yet another radical with formation of a diamagnetic compound:

$$\dot{\text{R}} + \text{R—NO} \rightarrow \text{R—N(O}\cdot\text{)—R} \xrightarrow{\dot{\text{R}}} \text{R—N(OR)—R}\ .$$

The rate constants for the reactions of nitroxy-radicals with solvated electrons, H atoms, and the radicals $\dot{O}H$ and $\dot{C}H_3$ reach 10^9–10^{10} litre $mole^{-1}$ s^{-1} [8,96,158] and those for the reactions with R$\dot{C}$HOH radicals reach 10^8 litre $mole^{-1}$ s^{-1}. This property of nitroxy-radicals has served as a basis for their employment as radical counting agents[8,97], which must be taken into account in the determination of the amount of unstable radicals captured by the spin-trapping agent, because one molecule of the spin-trapping agent can capture two radicals. In the case of nitrones the first radical adds to the carbon atom of the nitrone group and the second adds to the oxygen atom[98].

In addition, it has been noted[1,99,100] that, as a result of the trapping of unstable radicals by nitrones, the hydrogen atom in the radical adduct becomes readily mobile and can be abstracted by certain radicals and the nitrone formed in this case can capture radicals:

$$\text{Ph—CH(R)—N(O}\cdot\text{)—Bu-t} \xrightarrow{\dot{\text{R}}} \text{Ph—C(R)=N(O)—Bu-t} + \text{RH}\ .$$

For example, in the study of the radical adducts of PBN with chlorine and fluorine atoms, two types of nitroxy-radicals were detected in the EPR spectra[1,101]: Ph–CH(Cl)–N(Ö)–Bu-t and Ph–CCl_2–N(Ö)–Bu-t.

III. THE APPLICATION OF SPIN-TRAPPING AGENTS IN THE STUDY OF RADICAL PROCESSES

1. THE MECHANISMS OF ORGANIC REACTIONS

(a) Oxidation of Organic Compounds

In the majority of studies carried out with the aid of spin-trapping agents, the formation of radicals in the interaction of various oxidants with organic compounds of many classes has been investigated. Nitrosobenzene and TNB have been used to study the mechanism of the oxidation of aromatic compounds by nickel peroxide dispersed in benzene[19,102]. The aromatic hydrocarbons $ArCHR_2$ or Ar_2CHR with mobile methylene hydrogen atoms are oxidised with formation of radicals of the benzyl type if the substituents R are phenyl, cyano-, acyl, acyloxy-, alkoxy-, or allyl groups. The radicals formed in the oxidation of aromatic amines and phenols[19], diphenylacetonitrile, carbazole, acetonylacetone, and acetamide[102] by nickel peroxide have also been investigated.

Lead tetraacetate and Ce^{4+} ions oxidise 1,3-dicarbonyl compounds, for example acetylacetone and it is suggested that the first stage of the process is electron transfer from the ketone to the oxidant cation. Adducts with radicals of the type R–CO–$\dot{C}$H–CO–R have been observed in the presence of TNB.[18,32] On excitation with ultraviolet light $Pb(AcO)_4$ and thallium(III) ions give rise to the oxidative decarboxylation of carboxylic acids. When TNB and 2-methyl-2-nitroso-3-butanone in CH_2Cl_2 were used at a low temperature (–40°C), adducts with primary alkyl radicals were detected[18,31] and ultraviolet irradiation at 20°C led to the formation of adducts with the secondary radicals R$\dot{C}$HCOOH.

Most attention has been devoted to the mechanisms of the oxidation of alcohols. It has been established with the aid of spin-trapping agents that the mechanisms of the action of various oxidants are not the same. Uranyl nitrate, the radicals t-Bu$\dot{O}$ and $\dot{O}H$, and benzophenone in the triplet state abstract an α-hydrogen atom from the alcohol molecule and the EPR spectra show lines due to the adducts of hydroxyalkyl radicals with TNB, PBN, and DMPO[1,2,33,55,59,103].

In the photochemical oxidation of isopropyl and diphenylmethyl alcohols by benzophenone in the triplet state, the adduct of an H atom was detected together with the TNB adducts of the radical $(CH_3)_2\dot{C}OH$ under the conditions of continuous generation of radicals[30,33]. The appearance of the adduct with atomic hydrogen was explained[1,30,33] by electron transfer from the radical $(CH_3)_2\dot{C}OH$ to the TNB molecule with subsequent protonation of the radical-anion t-$BuNO^{\cdot-}$:

$$(CH_3)_2\dot{C}OH + \text{t-BuNO} \rightarrow (CH_3)_2CO + \text{t-BuNO}^{\cdot-} + H^+$$
$$\text{t-BuNO}^{\cdot-} + (CH_3)_2CHOH \rightarrow \text{t-BuN(}\dot{\text{O}}\text{)H} + (CH_3)_2CHO^-\ .$$

However, one should note that the adducts of TNB with H atoms can be formed not only via electron transfer but also as a result of secondary reactions: (1) the disproportionation of the adducts of TNB with the radicals $(CH_3)_2\dot{C}OH$ involving the formation of the hydroxylamine derivative R–N(OH)–Bu-t; (2) the reaction of t-butylhydroxylamine with a TNB molecule to form an adduct with an H atom. These reversible reactions have been observed[28,29]:

$$\text{t-Bu—N(H)—OH} + \text{t-BuNO} \rightleftarrows 2\,\text{t-Bu—N(O}\cdot\text{)—H}\ .$$

The abstraction of an α-hydrogen atom from the alcohol molecule had been suggested earlier also when variable-valence metal ions[104] and persulphate ions[105] are used as oxidants, although such powerful oxidants can convert alcohols into alkoxy-radicals. R$\dot{O}$ radicals could not be detected by EPR in the thermal and photochemical oxidation of alcohols even when a flow technique was used[106–108]. Owing to their high reactivity, R$\dot{O}$ radicals reacted with the alcohol, forming the radicals R$\dot{C}$HOH, which were detected by EPR. Only the use of spin-trapping agents made it possible to show that the oxidation of alcohols (methanol, ethanol, propanols, butanols, 2-phenylethanol, and cyclohexanone) by oxidants such as lead tetraacetate,

silver nitrate, and potassium persulphate leads to the formation of alkoxy-radicals [18,55,59].

The reactions of ȮH and t-BuȮ radicals have been studied in a number of investigations. The t-BuȮ radicals were generated by the photolysis of alkyl nitrites and also in the thermal decomposition of t-butyl peroxalates and t-butyl hydroperoxide. The oxidation of aldehydes has been investigated with the aid of TNB, nitrosobenzene, and the *N*-oxides of aromatic nitriles [34,39,73]. In the absence of aldehydes the adducts of t-BuȮ radicals are formed and in the presence of aldehydes the spin-trapping agent captures the acyl radicals R–Ċ=O. In addition TNB has been used to study the reactions of t-BuȮ radicals with sulphides, $CHCl_3$, acetate and malonate esters, toluene, ethylbenzene, and isopropylbenzene. The abstraction of the most mobile hydrogen atom was observed in all cases [16,33,34]. The reactions of ȮH radicals with ketones [31] and with sulphoxides and sulphones [32] have been studied with the aid of TNB. The ȮH radicals were generated by the photolysis of H_2O_2 solutions. In the reaction with ketones, mainly the adducts of TNB with the radicals formed by the abstraction of an α-hydrogen atom relative to the carbonyl group were observed. The reactions of ȮH radicals with sulphoxides and sulphones result in the formation of various alkyl and aryl radicals.

Photochemical oxidation by benzophenone in the triplet state was studied with the aid of TNB. Not only alcohols but also amines, phenols, sulphides, thiols, ethers, and hydrocarbons have been investigated under the conditions of the continuous generation of radicals in the resonator [30]. In some cases the spin-trapping agents themselves were involved in photochemical oxidation. The oxidation of alkenes in photolysis by red light in solution in the presence of TNB and oxygen proceeds via the following mechanism according to the authors [10]:

$$t\text{-BuNO} \xrightarrow{h\nu} t\text{-BuNO}^* \xrightarrow{O_2} t\text{-Bu}(\dot{O})\text{N}(\dot{O})\text{O}\cdot$$

$$t\text{-Bu}(\dot{O})\text{N}(\dot{O})\text{O}\cdot + PhCH{=}CH_2 \rightarrow t\text{-Bu}(\dot{O})\text{N}(\dot{O})\text{O}\text{–}CH(Ph)\text{–}\dot{C}H_2$$

$$\rightarrow t\text{-BuNO} + PhC(=O)H + CH_2O \ .$$

Benzaldehyde and formaldehyde were indeed detected in the reaction products. However, one cannot rule out the possibility of the formation of excited singlet oxygen which behaves as an oxidising agent:

$$t\text{-BuNO}^* + O_2 \rightarrow t\text{-BuNO} + O_2^*(^1S) \ .$$

(b) Photolysis of Organic Compounds

It has been shown that the photolysis of aryl iodides in the presence of TNB leads to the formation of aryl radicals which react with TNB to form adducts stable at room temperature. This method is convenient for the synthesis of aromatic nitroxy-radicals [31].

In the photolysis of halogenomethanes of the type CX_4, CHX_3, and CH_2X_2 (where X is a halogen atom) the radicals are formed as a result of the homolytic dissociation of the C–X bond [22,23,25,38,101,109]. The adducts with the $\dot{C}Cl_3$ and $\dot{C}HCl_2$ radicals can be conveniently detected when perfluoro-t-nitroso-butane is used [22,109]. In the presence of TNB, adducts with the X–Ċ=O radicals were detected together with the adducts of $\dot{C}X_3$ radicals [22–25,38,109]. The formation of the former is indicated by secondary reactions of the TNB radical adducts [23,25,38]. The study of the mechanism of the formation of the adducts of TNB with the radicals X–Ċ=O showed that, in the presence of an alcohol or dimethylamine, the nitroxy-radicals X–C(=O)–N(·)–Bu-t (X = Cl or Br) are transformed into the radicals RO–C(=O)–N(·)–Bu-t, whose structure has been established with the aid of nitrosoperdeutero-t-butane [23–25] and also by means of independent synthesis.

Photolysis of organometallic compounds of lead, tin, and mercury in the presence of PBN leads to the formation of adducts with radicals of the alkyl, phenyl, or benzyl types, depending on the nature of the substituents. It was found that the capacity for dissociation of the bond with the metal diminishes in the sequence phenyl > alkyl > acetate (or halogen) [1,47]. Adducts with the short-lived radicals $CH_3C(=O)\dot{O}$ and $PhC(=O)\dot{O}$ were detected in the photolysis of lead acetate and mercury benzoate, but the same adducts can arise also as a result of the addition of acetate and benzoate ions to PBN (see Section II, subsection 3).

Adducts with phenyl radicals were detected in the photolysis of organometallic compounds of the type Ph_3M (M = N, As, Sb, or Bi) in the presence of PBN, but the adducts of radicals containing a metal atom (Ph_2M) [100], which should have appeared if the decomposition proceeds via the mechanism

$$Ph_3M \xrightarrow{h\nu} Ph\cdot + Ph_2M \ ,$$

were absent.

Adducts with radicals of the acyl type RO–Ċ=O were detected in the photolysis of R–Hg–C(O)OR in the presence of BNB. [111] Adducts with ȮH radicals [67] were found in the photolysis of dilute H_2O_2 solutions in the presence of PBN and DMPO [67], while in concentrated H_2O_2 solutions adducts of $H\dot{O}_2$ radicals were detected. One cannot rule out the possibility that the latter appear as a result of the chemical reaction of H_2O_2 with the trapping agent.

The radical products of the photochemical and thermal decomposition of *p*-tolyl arylazosulphones were investigated with the aid of TNB and PBN. [50] It has been suggested that these compounds decompose via the mechanism

$$Ar\text{–}N{=}N\text{–}S(=O)(=O)\text{–}C_6H_4\text{–}CH_3 \rightarrow Ar\cdot + N_2 + \dot{S}O_2\text{–}C_6H_4\text{–}CH_3 \ .$$

The adducts with aryl radicals was identified [50] with the aid of PBN but the adducts with the radicals $H_3C\text{–}C_6H_4\text{–}\dot{S}O_2$ were not detected. In the presence of TNB a triplet was observed in the EPR spectra, which the authors attributed to the adduct of TNB with the radicals $H_3C\text{–}C_6H_4\text{–}\dot{S}O_2$.

The study of the thermal and photochemical rearrangement of acetophenone diphenylmercaptal with the aid of TNB showed that the process proceeds via a radical stage:

$$PhC(PhS)_2CH_3 \rightarrow Ph\dot{C}(PhS)CH_3 + PhS\cdot \ .$$

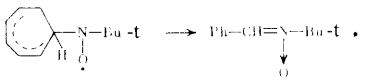
The adducts of TNB with both radicals have been detected. In the presence of O_2, adducts with the $PhC(\dot{O})\text{–}(PhS)CH_3$ and $PhC(PhS)_2\dot{C}H_2$ radicals were also observed [112].

The photolysis of TNB in the presence of diethyl α-halogenophosphonates leads to the formation of phosphorus-containing nitroxy-radicals [113] of the type t-Bu–N(·)–CH(R)–P(=O)$(OC_2H_5)_2$. Phosphorus-containing nitroxy-radicals can also be obtained from the nitroso-compound

$(CH_3)_2C(NO)-P(OEt)_2$, whose synthesis has been described [114].

(c) Other Types of Organic Reactions

It has been shown for the first time with the aid of TNB that, when tropylium tetrafluoroborate is reduced with zinc, the product is a tropyl radical, the EPR spectrum of the adduct of which with TNB is a triplet of doublets (a_N = 14.5 G, a_β^H = 2.2 G).[28] This nitroxy-radical is subsequently oxidised to PBN:

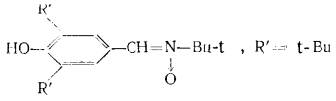


The dark reaction of tetranitromethane with nucleophiles (N_3^-, NO_2^-, OH^-, F^-, Cl^-, I^-, t-BuO^-, etc.) has been investigated with the aid of PBN.[48,115,116] According to the authors, there is electron transfer from the nucleophile to tetranitromethane. The adduct with the NO_2 radical was not detected, the benzoyl-t-butylnitroxy-radical, which is a PBN oxidation product, being formed instead.

The adducts of PBN with radicals derived from nucleophiles [t-BuO^-, $C(NO_2)_3^-$] were detected in the interaction of $FClO_3$ with nucleophiles [116]. In the presence of nucleophiles, the fluorine atom is captured. The formation of nitroxy-radicals was observed also in TNB solutions containing aromatic compounds and nucleophiles (OH^-, CH_3O^-)[48,117,118]. However, the authors' conclusions[48,115,118] are not unambiguous, since nitroso-compounds and nitrones can react with nucleophiles in the absence of oxidants, forming nitroxy-radicals[20,119,120] (Section II, subsection 3). The formation of the t-BuNO$^\cdot$ radical-ion has been noted, for example, in TNB solutions in the presence of t-BuOK [120].

Adducts of PBN with fluorine atoms have been detected in the products of the decomposition of NF_3O in benzene in the presence of PBN.[1] Since NF_3O is used in preparative chemistry as a fluorinating agent, the fluorination reaction may occur with participation of fluorine atoms. Adducts with chlorine atoms have been detected in the thermal decomposition of t-BuOCl in benzene in the presence of PBN [101].

The reaction of *N*-chlorosuccinimide with toluene-*p*-sulphonic acid has been investigated[69,121,122]. In the presence of the bifunctional trapping agent



the phenoxy-radical was detected and in the presence of PBN the product was found to be the radical PhC(O)N(O$^\cdot$)-Bu-t, arising, according to the authors [121], as a result of the oxidation of PBN by chlorine atoms or the succinimyl radical. The adducts of PBN with the succinimyl radical and chlorine atoms were not, however, detected. When t-butylmethylenenitrone and TNB were used as spin-trapping agents, the EPR spectra of the adduct of the succinimyl radical were detected[69,121,122]. The adducts of the succinimyl radical with TNB and MN also appeared in the photolysis of *N*-chloro- and *N*-bromo-succinimides in benzene, but in polar solvents the adducts were not detected [69].

The possibility of the radical rearrangement of $XCH_2\dot{C}HCCl_3$ to $XCH_2CH\dot{C}Cl_2$ (X = t-BuO or CCl_3) has been investigated [123]. In the presence of 2-methyl-2-nitroso-3-butanone the adduct with the radical $XCH_2\dot{C}HCCl_3$ was detected, while in the presence of TNB the product was the adduct with the radical $XCH_2CH\dot{C}Cl_2$. The adducts of both radicals with the same spin-trapping agent were not found, so that secondary reactions of the radical adducts probably take place in the system.

The radical arylation of disulphides has been studied in the presence of TNB. Phenyl radicals attack the disulphide at a sulphur atom and the EPR spectra contain lines due to the adducts of the radicals Ph$\dot{S}$ (triplet with a_N = 16.3 G) [159]:

$$\dot{Ph} + (PhS)_2 \rightarrow PhSPh + Ph\dot{S} \ .$$

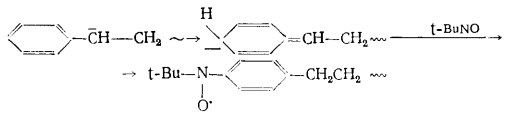
Spin-trapping agents have been used in the study of polymerisation processes[20,124-126]. By varying the concentration of the spin-trapping agent, it is possible to detect adducts with radicals having different degrees of polymerisation. At a high concentration of the spin-trapping agent (0.1 M and above) mainly radicals derived from the initiator are captured, while at low concentrations (0.001 M) polymeric radicals are captured. Radicals arising in the photolysis of TNB have been used to initiate the polymerisation of unsaturated phosphonic acid esters [124].

MN and TNB have been used [125] to investigate the polymerisation of styrene initiated by t-BuO$^\cdot$ radicals:

$$t\text{-}BuO^\cdot + PhCH=CH_2 \rightarrow Ph\dot{C}HCH_2O\text{—}Bu\text{-}t \ .$$

At a TNB concentration of 0.05 M the adduct with the radical $Ph\dot{C}HCH_2O$-Bu-t (a_N = 14.3 G, a_β^H = 2.3 G) was detected [125]. At low TNB concentrations, (0.001 M) adducts with the longer radicals Ph-$\dot{C}HCH_2(PhCHCH_2)_nO$-Bu-t ($a_N$ = 14.5 G, a_β^H = 3.3 G) were detected.

The spin-trapping agents TNB and PBN terminate the anionic polymerisation of styrene, methyl methacrylate, vinylpyridines, etc. with formation of stable polymeric nitroxy-radicals by the addition of an anion to a nitroso-compound or nitrone [20]:



This process is the simplest pathway to the formation of "spin-labelled" polymers [20]. Spin-trapping agents make it possible to synthesise nitroxy-radicals, the preparation of which in the usual chemical way involves considerable experimental difficulties. The application of nitrones in the synthesis of nitroxy-radicals was first described by Iwamura and Inamoto [5,6].

The electrochemical oxidation of the nitromethanes $C(NO_2)_3^-$, $CH_3C(NO_2)_2^-$, and $(CH_3)_2C(NO_2)^-$ was investigated with the aid of PBN [115,116]. In the reaction with $C(NO_2)_3^-$ the product was found to be an adduct whose spectrum showed splittings with a_N = 14.1 G and a_β^H = 4.2 G. The authors attributed this spectrum to the adduct of PBN with the $\dot{C}(NO_2)_3$ radical. Nitroxy-radicals of the same type are formed also in the photolysis of the anions of nitroso-compounds [115,116]. In the course of the electrochemical reduction of the benzenediazonium cation in the presence of PBN the product is an adduct with the phenyl radical [127]. One must note that nitrones and nitroso-compounds are effective electron acceptors [20,58,92,128,158] and can oxidise anions with formation of the corresponding radicals.

2. THE DETECTION OF RADICALS FORMED IN THE GAS PHASE

Spin-trapping agents can be used for the identification of radicals formed in the gas phase[51,61,129-131]. Both solid trapping agents and their vapours have been used for this purpose. The solid spin-trapping agent (PBN, NTB, or nitrosobenzene) was placed in the stream of gases emerging from the electric discharge and, after switching off the discharge, was transferred (in the absence of oxygen) to a suitable solvent and the EPR spectra of the nitroxy-radicals were observed. The nitroxy-radicals are highly volatile and can be frozen out in a trap cooled with liquid nitrogen[61,129,130].

When a gas discharge was allowed to act on D_2O vapour, H_2, D_2, CH_4, and NH_3, the adducts of PBN with H and D atoms and with the $\dot{O}H$, $\dot{O}D$, and $\dot{C}H_3$ radicals were detected[61]. In ammonia only the adducts with H atoms were found and the adducts with $\dot{N}H_2$ radicals were not detected. In a discharge in toluene adducts with radicals of the phenyl and benzyl type were found[60]. A study was also made of the pyrolysis of organosilicon compounds in the presence of PBN[130]. As in the thermal decomposition of t-BuOCl in benzene[101], in the gas-phase photolysis of this substance[129] the adducts of PBN with chlorine atoms and in addition the $PhCCl_2$–N(O)–Bu-t radical were detected. The gas-phase photolysis of alkyl iodides, ketones, and aldehydes has been studied[131]. Adducts with alkyl radicals were detected in the presence of solid PBN and in the presence of TNB in the vapour phase adducts with acyl radicals were found in the reactions with aldehydes and ketones. The radicals arising in cigarette smoke have been studied with the aid PBN[132].

The spin-trapping method has many advantages compared with the direct gas-phase EPR method[133]. In particular, not only adducts with monatomic and diatomic radicals (the usual species for which EPR is used in the gas phase) but also those with radicals such as $\dot{C}H_3$, $\dot{C}_2H_5$, t-Bu$\dot{O}$, $\dot{P}h$, $Ph\dot{C}H_2$, and R–$\dot{C}$=O have been detected.

3. THE APPLICATIONS OF SPIN TRAPPING AGENTS IN CHEMICAL KINETICS

The high stability of radical adducts makes it possible to use spin-trapping agents in kinetic studies. The reaction of a spin-trapping agent with a radical cannot as yet be observed directly in view of its high rate and the rate constants for these reactions are therefore determined by the method of steady-state concentrations.

The rate constants for the trapping of PhCO$\dot{O}$ radicals by certain PBN derivatives[134] were determined with the aid of the galvinoxy-radical as a competing acceptor. The rate constant for PBN is 4.0×10^5 litre mole^{-1} s^{-1}. The rate constant for the decomposition of di-t-butyl peroxalate into t-Bu$\dot{O}$ radicals ($k = 6.8 \times 10^{-5}$ s^{-1} at 35°C) and the activation energy, which is 30 kcal mole^{-1}, were obtained by the same method. The above values agree with the results obtained by other procedures.

The absolute rate constants for the trapping of t-Bu$\dot{O}$ radicals by various spin-trapping agents have been obtained taking into account the known rate constants for the abstraction of hydrogen by t-Bu$\dot{O}$ radicals from cyclohexane and toluene[68]. Under these conditions, the EPR spectra of the adducts of t-Bu$\dot{O}$ radicals and alkyl radicals arising in the competing reaction of t-Bu$\dot{O}$ with the hydrocarbon were recorded at the same time. Since the EPR spectra of various PBN radical adducts overlap markedly, DMPO was used as the spin-trapping agent (Section II, subsection 3), since the EPR parameters of the adducts of this trapping agent with R$\dot{O}$ radicals differ markedly from those of the adducts with alkyl radicals. The rate constant for the trapping of t-Bu$\dot{O}$ radicals by DMPO molecules proved to be 5×10^8 litre mole^{-1} s^{-1}.[68] The rate constants for the reactions of t-Bu$\dot{O}$ radicals with various spin-trapping agents (Table 7) were determined with the aid of the competition of two trapping agents (one of which was DMPO) for the t-Bu$\dot{O}$ radical.

The rate constants for the trapping of t-BuO–$\dot{C}$=O radicals by TNB and for the decomposition of the adducts of TNB with the t-Bu$\dot{O}$ radical ($k_1 = 1.1 \times 10^{-3}$ s^{-1}) have been estimated[59]. The ratio of the rate constants for the reactions of the t-Bu$\dot{O}$ radicals with ethylbenzene and toluene[33], determined with the aid of TNB, is 8.6 ± 1.0.

The rate constants for the trapping of $\dot{P}h$ and PhCO$\dot{O}$ radicals by PBN molecules, which are 1.2×10^7 and 4.0×10^7 litre mole^{-1} s^{-1} respectively at 20°C, have been measured[135,136]. Previously, unduly low values of the order of 10^5–10^6 litre mole^{-1} s^{-1} had been obtained for these constants[134], since an approximate rate constant for the decarboxylation of PhCO$\dot{O}$ radicals, equal to 10^3–10^4 s^{-1}, had been used in the calculations. Using PBN, 5.0×10^5 s^{-1} was obtained for this constant[135].

The rate constants for the attachment of phenyl radicals to benzene with formation of phenylcyclohexadienyl radicals[135] as well as the rate constants for the abstraction of H atoms from alcohol molecules by phenyl radicals[136] have been determined with the aid of PBN (Table 8). The rate constants for the fragmentation of acyl radicals in benzene have been found by the spin trapping method[39].

Table 8. Reaction rate constants determined with the aid of spin-trapping agents.

Reaction	Rate constant	Reaction conditions	Refs.
PhCO$\dot{O}$ → $\dot{P}h$ + CO_2	5×10^5 s^{-1}	20°C, benzene	135
$\dot{P}h$ + C_6H_6	7.8×10^4 litre mole^{-1} s^{-1}	20°C, benzene	135
$\dot{P}h$ + CH_3OH	1.4×10^5 litre mole^{-1} s^{-1}	20°C, alcohol	136
$\dot{P}h$ + C_6H_5OH	2.3×10^5 litre mole^{-1} s^{-1}	20°C, alcohol	136
$\dot{P}h$ + 2-propanol	4.1×10^5 litre mole^{-1} s^{-1}	20°C, alcohol	136
R–$\dot{C}$=O → $\dot{R}$ + CO			
R = CH_3, n-C_3H_7	~1 s^{-1}	40°C, benzene	39
R = iso-C_3H_7	3.9×10^3 s^{-1}	40°C, benzene	39
R = t-Bu	5.2×10^4 s^{-1}	40°C, benzene	39
R = $PhCH_2$	7×10^6 s^{-1}	40°C, benzene	39

The study of the radiolysis of alcohols yielded the rate constants for the trapping of $CH_3\dot{O}$ and $C_2H_5\dot{O}$ radicals by PBN molecules at 20°C: $k(CH_3\dot{O} + PBN) = 1.2 \times 10^8$ litre mole^{-1} s^{-1} and $k(C_2H_5\dot{O} + PBN) = 2.0 \times 10^8$ litre mole^{-1} s^{-1}.[58,139] The absolute rate constants for the reactions of R$\dot{O}$ radicals with alcohols, determined by pulse radiolysis, were used in the calculations[137,138]: $k(CH_3\dot{O} + CH_3OH) = 2.62 \times 10^5$ litre mole^{-1} s^{-1} and $k(C_2H_5\dot{O} + C_2H_5OH) = 1 \times 10^6$ litre mole^{-1} s^{-1}. The rate constant for the trapping of $CH_3\dot{O}$ by TNB molecules proved to be 1.3×10^8 litre mole^{-1} s^{-1} at −45°C in methanol [method based on the use of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (TMPD) as a competing acceptor[157]].

Thus the spin-trapping method makes it possible to obtain extensive information about the reactivities of radicals.

4. THE USE OF THE SPIN-TRAPPING METHOD IN RADIATION CHEMISTRY

The earlier procedures for the investigation of radicals in radiation-chemical processes suffer from serious disadvantages. The difficulty of analysing the EPR spectra of radicals in the solid phase has already been noted. The EPR spectra in the liquid phase under the influence of an electron beam also have a low signal-to-noise ratio and the shortest-lived radicals are not detected[56]. Radicals of the type RȮ and ȮH are not detected in the liquid phase owing to their short relaxation times.

The possibility of using the spin-trapping method for the investigation of radicals formed in solid-phase radiolysis was first demonstrated by Lagercrantz and Forschult[37]. The solid substances subjected to preliminary γ-irradiation were dissolved in a weakly alkaline TNB solution. It was observed that the $\dot{C}H_2COO^-$ radical-ions are stabilised in sodium acetate and glycine, while radicals of the type R–ĊHCOOH are stabilised in alanines, potassium malonate, and succinic and glutamic acids. When the solid was dissolved, adducts of these radicals with TNB were formed. After dissolution of γ-irradiated Na_2HPO_3 the adduct of TNB with the $\dot{P}O_3^{2-}$ radical-ion was detected and the adduct with the ṖOH(O) radical was found in γ-irradiated NaH_2PO_2.[140,141]

Spin-trapping agents have been used most frequently in the liquid phase. Adducts with $\dot{C}Cl_3$ radicals and chlorine atoms have been found in CCl_4 irradiated in the presence of PBN,[1] which agrees with the presence of C_2Cl_6 and Cl_2 in the radiolysis products.

In order to identify the radicals arising in aqueous solutions or organic compounds on γ-irradiation, TNB was used[66,94,142]. Adducts of the $\dot{C}H_2OH$ radical (a_N = 15.5 G, a_β^H = 6.1 G), which are stable at 20°C, were detected in 0.5 M aqueous solution of methanol in the presence of TNB.[94] Well resolved EPR spectra of the adducts of TNB with radicals of the type –ĊH–N= were obtained in dipeptides and nucleic bases γ-irradiated in aqueous solutions at 20°C.[94,142]

Thiols RSH (R = Me, Et, n-Br, iso-Pr, or n-Bu), γ-irradiated at low temperatures (–73°, –102°C) in the liquid phase have been investigated[36] with the aid of TNB. The adducts of TNB with thiyl radicals were identified. They have well resolved EPR spectra, which distinguishes them favourably from the EPR spectra of these radicals in the solid phase, where the hyperfine structures are not resolved and the identification is not unambiguous[155]. For example, the spectra of the adducts with $\dot{C}H_3S$ radicals consist of a triplet of quartets (a_N = 18.9 G, a_β^H = 1.2 G).

Water subjected to an electron beam has been investigated[66] at 20°C with the aid of DMPO, TNB, and PBN. The adducts of the above spin-trapping agents with ȮH radicals and H atoms were detected (the spectral parameters are presented in Tables 2, 5 and 6). In the case of DMPO and TNB hydrogen atoms and solvated electrons lead to the same adduct, since the radical-anion formed as a result of the trapping of electrons is protonated in water:

$$DMPO + e^- \rightarrow DMPO^- \xrightarrow{H_2O} DMP\dot{O}{-}H + OH^- .$$

The radiolysis of benzyl alcohol by means of an electron beam has been investigated in the presence of TNB.[143] The formation of benzyl radicals $Ph\dot{C}H_2$ and the radicals PhĊHOH was demonstrated. The addition of electron-accepting agents showed that the benzyl radicals are formed in the reaction of electrons with the alcohol and the t-BuN(Ȯ)–H adduct detected arises, according to the authors, as a result of electron transfer from the PhĊHOH radicals:

$$\text{t-BuNO} + Ph\dot{C}HOH \rightarrow \quad \text{t-BuN(Ȯ)H} + PhCHO .$$

The adducts with $PhCH_2\dot{O}$ radicals were not detected. The TNB concentration employed (0.01 M) is apparently too low for the effective competition of TNB for the $PhCH_2\dot{O}$ radical[143].

Ethylene glycol γ-irradiated in the liquid and solid phases has been studied with the aid of TNB[144–146]. A triplet of doublets (a_N = 15.4 G, a_β^H = 1.5 G) of the adduct with the $HOCH_2\dot{C}HOH$ radical as well as a triplet of triplets (a_N = 14.4 G, a_β^H = 5.1 G),[146] referring to the adduct with the $\dot{C}H_2OH$ radical, and the 3 × 3 × 2 multiplet (a_N = 15.5 G, a_β^H = 9.1 G, and a_γ^H = 0.6 G), identified as the spectrum of the adduct with the $\dot{C}H_2CHO$ radical, were observed in the EPR spectra. The identification of the last adduct is confirmed[146] by the splitting by γ-protons and the magnitude of the splitting by β-protons, which is characteristic of adducts with radicals of the type $\dot{C}H_2R$ (Table 2). The EPR spectrum of ethylene glycol irradiated at –196°C without spin-trapping agents shows only a poorly resolved triplet and singlet due to stabilised electrons.

The radiolysis of alkanes[91] and aromatic hydrocarbons[13,147] has been studied with the aid of spin-trapping agents. Using nitrosodurene and PBN, phenyl radicals were identified in benzene γ-irradiated at 20°C and benzyl radicals and radicals of the phenyl type were identified in toluene[147]. $t\text{-}Bu_2N\dot{O}$ radicals are formed in a yield of 1.5 radicals/100 eV in benzene, toluene, and *o*-xylene irradiated at 20°C in the presence of 0.1 M TNB.[13,147] It has been shown that the radicals $t\text{-}Bu_2N\dot{O}$ are formed as a result of the transfer of excitation from the aromatic hydrocarbon to the TNB molecule and yields of the excited molecules of these hydrocarbons were measured and found to be 2.5 ± 0.5 molecules/100 eV. Thus certain spin-trapping agents can trap not only radicals but also excited species and can be used for the quantitative determination of the yield of excited molecules.

The γ-radiolysis of nitriles has been studied in the liquid phase in the presence of PBN.[160] $\dot{C}H_2CN$ radicals in acetonitrile, H atoms and $CH_3\dot{C}HCN$ radicals in propionitrile, $\dot{C}H(CN)_2$ radicals in malononitrile, and H atoms and ĊN and $\dot{C}H_2CH_2CN$ radicals in succinonitrile have been identified. Splitting by γ-protons has been observed in the EPR spectra of the adducts of PBN with the radicals $\dot{C}H_2CN$ and $\dot{C}H(CN)_2$ (Table 5).

The radiolysis of alcohols in the liquid and solid phases has been studied in greatest detail by the spin-trapping method[11,12,27,35,40,45,57,58,90–92,139,148–150]. TNB, PBN, and BNB served as the spin-trapping agents. The formation of alkoxy-radicals and H atoms in methanol, ethanol, propanols, and t-butyl alcohol, irradiated by γ-rays and electrons in the liquid phase, was demonstrated for the first time in radiation chemistry. For comparison, we may state that neither H atoms nor RȮ radicals were detected in the study of frozen alcohols[155] nor were they observed directly under an electron beam in the liquid phase[108]. After γ-irradiation in the liquid phase in the presence of TNB, hydroxy-alkyl radicals were detected in methanol, ethanol, 1-propanol, and 2-propanol, while adducts of NTB and H atoms, arising as a result of the trapping of both H atoms and electrons with subsequent

protonation of the t-BuNO$^{\cdot-}$ radical anions, were found after exposure to an electron beam:

$$\text{t-BuNO}^{\cdot-} + \text{ROH} \rightarrow \quad \text{t-Bu(O)} - \text{H} + \text{RO}^- .$$

An analogous electron capture process takes place in the case of BNB. Irradiation of BNB solutions in methanol and ethanol at −196°C leads to the formation of BNB radical-anions which are converted quantitatively into BNB adducts with H atoms on raising the temperature to −155°C.[45]

Analysis of literature data [11,12,35,45,90,94] has shown that TNB and BNB can be used in the radiolysis of alcohols only for the identification of radicals. Complications arise owing to secondary reactions between radical adducts [12] and the low efficiency of the trapping of certain radicals by BNB. As a result of the reaction between TNB adducts with $\dot{C}H_2OH$ radicals and H atoms, the yield of $\dot{C}H_2OH$ and $CH_2\dot{C}HOH$ adducts is low under continuous generation conditions in an electron beam [27,90] and there is a complete absence of $\dot{C}H_2OH$ adducts in methanol γ-irradiated at −80°C [11,35] in the presence of a high TNB concentration. In the case of BNB the adducts of the latter with $CH_3\dot{C}HOH$ radicals were hardly detected[45].

Quantitative yields of primary radicals in the radiolysis of liquid and solid alcohols have been measured successfully with the aid of PBN [58,92,139]. Solvated electrons are fully captured by this trapping agent for [PBN] ≥ 0.1 M and do not contribute to the overall yield of radicals at 20°C, since the adducts of PBN with an electron decompose at temperatures above −150°C without the formation of any radical adducts [92]. The yields of RȮ radicals were determined using irradiation in the presence of O_2. RȮ radicals do not react with O_2, while R$\dot{C}$HOH radicals and H atoms do react with O_2 with high rate constants, forming peroxy-radicals which do not give rise to stable adducts with PBN and are not detected in EPR spectra [92]. The yields of RȮ and R$\dot{C}$HOH radicals and H atoms in methanol, ethanol, 1-propanol, and 2-propanol, γ-irradiated at temperatures from +20° to −196°C, have been measured by the method of competitive kinetics [58,92,130]. For example, in methanol at 20°C $G(CH_3\dot{O}) = 2.5$, $G(H) = 0.6$, and $G(\dot{C}H_2OH) = 3.1$ radicals/100 eV, while in ethanol $G(C_2H_5\dot{O}) = 1.6$ radicals/100 eV. The yields of RȮ radicals obtained with the aid of the spin-trapping method agree with indirect determinations of the corresponding yields by pulse radiolysis [137,138] and with the calculation based on the final products.

Apart from t-BuȮ radicals adducts with the $\dot{C}H_2(CH_3)_2$. COH, $\dot{C}H_3$, and t-Bu̇ radicals were detected in γ-irradiated t-butyl alcohol [11,40]. It was shown [40] that $\dot{C}H_3$ radicals appear only in the decomposition of t-BuȮ radicals and t-Bu̇ radicals do not arise in the radiolysis of alcohol itself, being formed in the decomposition of the spin adducts of TNB and nitrosodurene with t-BuȮ radicals. It has been stated that the use of t-butylmethylenenitrone for the study of the radiolysis of polar systems is promising [70].

Thus the following problems can be solved with the aid of spin-trapping agents: (1) identification of short-lived radicals; (2) determination of the quantity of unstable radicals; (3) determination of the kinetic characteristics of the trapped radicals. In addition, spin-trapping agents can be used for the synthesis of spin-labelled compounds and for the inhibition of chain processes. Spin-trapping agents are used with a high degree of efficiency in various branches of chemistry, primarily in the study of oxidation and reduction reactions, radical rearrangements, catalytic processes, and polymerisation. Another field where they are used involves the chemistry of high energy processes (radiation and laser chemistry, photochemistry, ultrasonic chemistry, plasma chemistry, and mechanochemistry), in the majority of which there are radical stages. The spin-trapping method can prove to be of significant assistance in biological research, particularly in radiobiology.

The spin-trapping method has significant advantages over other versions of the EPR method, primarily because of the possibility of detecting unstable radicals in processes where the radical concentrations are too low for investigation by other methods. The main advantages is the recording of EPR spectra directly in the liquid phase, which makes it possible to increase appreciably the resolving capacity of EPR and to facilitate the identification of radicals compared with the solid phase. Different spin-trapping agents can be used to identify the same radical (Table 1).

The spin-trapping method also suffers from certain disadvantages associated mainly with the fact that a new compound (the spin-trapping agent) is introduced into the test system. In order to eliminate the uncertainty caused by introducing the spin-trapping agent, it is necessary to investigate independently its behaviour in the given system acted upon by the particular procedure. Naturally, one must carry out an additional study of the stability of the radical adducts and the possibility of their participation as free radicals in the test process itself.

The data presented in the review permit certain recommendations for the selection of spin-trapping agents: 1. It is desirable that the spin adducts should have the simplest EPR spectrum with the smallest possible overlapping of lines due to different radicals. 2. The chosen spin-trapping agents should not interact with the test systems. 3. The spin adducts should be fairly stable. 4. The spin-trapping agent should not itself give rise to radical adducts under the influence of light.

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Donor-Acceptor Interactions between Non-silver Information Recording Processes

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The use of non-silver layers based on intermolecular charge-transfer complexes (CTC) for the recording of information, the recording of the influence of light, and for microfilming is examined. The processes are based on the ability of the CTC to dissociate following the absorption of light with formation of products whose absorption spectrum is different from that of the initial films incorporating the CTC. General postulates concerning the mechanism of the photodissociation of the CTC are described and the characteristics of the photochemical reactions of specific systems used as light sensitive materials are considered.
The bibliography includes 142 references.

CONTENTS

I. Introduction 746
II. Conditions governing the photodissociation of charge-transfer complexes 747
III. The limiting light sensitivity of the layers in the absence of image intensification 749
IV. Light-sensitive charge-transfer complexes based on organic systems 749
V. Light-sensitive charge-transfer complexes based on organometallic compounds 753

I. INTRODUCTION

Organic systems whose physicochemical properties change under the influence of light have been widely investigated in recent years. Compounds or compositions whose optical properties change as a result of illumination are used to record images[1-4].

Light-sensitive layers based on organic materials are characterised by a high resolving capacity, the possibility in many instances of carrying out repeated recording-deletion cycles, the absence of chemical development and fixing stages, and the development (intensification) of the image on exposure or by simple physical methods (for example, by heat treatment) and hence the possibility of obtaining an image in real time, the elimination of expensive silver from the recording process, and many other valuable properties. At the same time the sensitivity of organic layers is lower by several orders of magnitude than that of silver bromide photographic materials. At the present time all the above factors make such materials promising in copying and special-purpose photography requiring a high resolution. The existing monographs and reviews deal in detail with the mechanisms of the photochromic transformations in organic compounds[1,2,5], the diazo-coupling reaction for diazonium salts in connection with their use in diazo-printing and in the vesicular process[6-10], as well as the physicochemical principles of the electrophotographic process[11,12].

This review discusses the characteristics of the changes under the influence of light in the chemical and optical properties of systems based on charge-transfer complexes (CTC). Two- or multi-component compositions, in which the primary stage of the complex process involving a change in the positions of the optical absorption bands is electron transfer from the donor component of the CTC to the acceptor component, have been examined. The special interest in intermolecular complexes is due to two factors. The first (the presence of an intermolecular bond) rules out the diffusion-dependent limitation of the rate of the photochemical reaction between two molecules. The second (ionisation of the donor component) corresponds to the absorption of a single light quantum, i.e. does not require high-intensity light sources and, depending on the nature of the selected components as well as the properties of the film-forming medium, can occur under the influence of light at wavelengths from 250 to 1500 mm. Systems based on CTC are beginning to find practical applications in the recording of images as a result of their high rate of colour change and the possibility of optical development[13-16] and thermal fixing[17].

The need to obtain materials whose colour changes under the influence of light requires the compounds to have a system of conjugated bonds. In these compounds the delocalised π electrons, characterised by a close proximity of allowed energy levels, are responsible for absorption in the visible and near ultraviolet and infrared regions. The colour of organic molecules is determined by the size of the conjugation system in combination with the presence of electron-donating and electron-accepting groups and their chemical composition[18-20]. The greatest displacement of the optical absorption bands is due to the change in the size of the continuous conjugation regions[18].

The dependence of the position of the optical absorption band on the size of the conjugated bond system was obtained by Kuhn[21-23] for cyanine dyes. It was established that, in symmetrical molecules with equal lengths of single and double bonds, the energy levels are distributed monotonically and correspond to the following relation between the position of the optical absorption maximum and the number of units N in the conjugated chain:

$$\lambda_{max} = \frac{8mcl^2}{h} \cdot \frac{N^2}{N+1}, \qquad (1)$$

where l is the length of a single chain unit. Owing to the difference between the lengths of single and double bonds, the energy spectrum of asymmetric molecules corresponds to an increased distance between the highest occupied and highest unoccupied levels compared with the distances between both highest occupied and lowest unoccupied orbitals. Such distribution of levels is characteristic of many conjugated molecules, which is the reason for the appearance of a spectrum in the long-wavelength region when the molecule is converted into a radical-cation or a radical-anion.

A shift of the absorption spectrum from the visible to the ultraviolet region accompanies the dissociation of the system of conjugated bonds on conversion of thiazine, triphenylmethane, and other dyes into their leuco-forms[18, 24-26, 13-15] and of xanthene dyes into the lactone form[27-31].

Certain specific properties of the CTC, which must be taken into account in selecting the components of the complex, are analysed below. These are the spin state at the dissociative level for complexes of different types as well as the region of maximum light sensitivity under the conditions corresponding to different ways of exciting the system.

II. CONDITIONS GOVERNING THE PHOTODISSOCIATION OF CHARGE-TRANSFER COMPLEXES

Since 1952, when Mulliken surveyed the accumulated data on the donor–acceptor interaction and described the phenomenon for the first time in quantum-chemical terms (in the gas approximation), numerous original papers, reviews, and monographs have been devoted to this field of study[32-39].

According to the ideas developed by Mulliken and Person[33], an intermolecular bond is formed in a system incorporating an electron donor (D) and acceptor (A) as a result of the mixing of the state in which there is only a van der Waals interaction (DA) between D and A and the dative state ($D^{+}-A^{-}$) in which the electron is fully transferred from the donor to the acceptor. The residence time of the system in each state $\tau \simeq h/W_{01} \simeq 10^{-13}-10^{-14}$ s,[40] since the Planck constant $h = 4.2\times10^{-15}$ eV s and the integral $W_{01} = \int\varphi(DA).H.\varphi(D^{+}-A^{-})d\tau = 0.05-0.5$ eV, where $\varphi(DA)$ and $\varphi(D^{+}-A^{-})$ are the wave functions of the non-bonded and dative states respectively. Thus, as a result of the mixing of the states, a dipole $D^{+\delta}A^{-\delta}$ is formed, where δ is the degree of charge transfer. The experimental methods for the measurement of δ have been examined in detail[33,41]. The idea of charge transfer has been introduced by Hausser and Murrel[42] in a quantum-chemical description of the state of dimers comprising identical radical-ions, because the ionisation potential of a radical-ion is close to the electron affinity. In contrast to the dative state of the CTC, in the dimer, owing to the complete identity of the radical-ions, this state corresponds to a jump of two electrons (in a paired state) between radical-ions at a frequency which, as stated above is close to 10^{14} s^{-1} and not to a directional charge transfer from one radical-ion to another.

Fig. 1 presents a generalised energy diagram for donor–acceptor systems of different types. A characteristic feature of the CTC is that, owing to the mixing of the (DA) and ($D^{+}-A^{-}$) states, the energy level of the ground state W_N lies below the positions of its components W_0 and W_1 (section I, Fig. 1). The energy gain is

$$W_N - W_0 = -(W_{01} - W_0S_{01})^2/(W_1 - W_0); \quad (2)$$

for weak CTC, where $W_1 \gg W_0$ (section I*a*, Fig. 1); in the vicinity of $W_0 \simeq W_1$ (section I*b*, Fig. 1) we have

$$W_N - W_0 = -(W_{01} - W_0S_{01})/(1 + S_{01}) \quad (3)$$

if $W_1 \geqslant W_0$ and

$$W_N - W_1 = -(W_0 - W_1S_{01})/(1 + S_{01}) \quad (4)$$

if $W_0 \geqslant W_1$, for the "reverse" CTC, where $W_0 \gg W_1$ (section I*c*, Fig. 1), the energy gain is

$$W_N - W_1 = -(W_{01} - W_1S_{01})^2/(W_0 - W_1). \quad (5)$$

For CTC, the overlap integral $S_{01} = \int\varphi(DA).\varphi(D^{+}-A^{-})d\tau \simeq 0.01-0.1$.[43] The excited energy level W_V in CTC exceeds the components W_1 and W_0 by an amount

$$W_v - W_1 = (W_{01} - W_1S_{01})^2/(W_1 - W_0) \quad (6)$$

or

$$W_v - W_0 = (W_{01} - W_0S_{01})^2/(W_0 - W_1) \quad (7)$$

along sections I*a* and I*c* respectively. We have

$$W_v - W_1 = (W_{01} - W_1S_{01})/(1 - S_{01}) \quad (8)$$

for $W_1 \geqslant W_0$ (section I*b*) or $W_1 > W_0$ and

$$W_v - W_0 = (W_{01} - W_0S_{01})/(1 - S_{01}) \quad (9)$$

for $W_0 \geqslant W_1$.

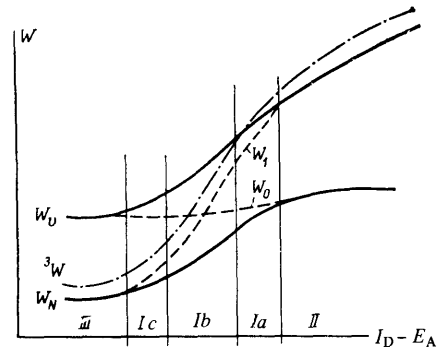


Figure 1. The energy scheme for electronic donor–acceptor complexes. Levels: ground (W_N), excited (W_V), triplet (^3W), non-bonding (W_0)(DA), and dative (W_1)($D^{+}-A^{-}$); I_D is the ionisation potential of the donor and E_A the electron affinity of the acceptor.

In a condensed medium the position of the level W_1 is determined by the relation

$$W_1 = I_D - E_A - Q - P + (C \pm K) \mp V,$$

where Q is the energy of the Coulombic attraction between radical-anions of different signs, P is the polarisation energy of the system, $C + K$ and $C - K$ are the energies of the Coulombic repulsion between unpaired electrons for the singlet and triplet orientations respectively, K is the exchange repulsion energy, and V the contribution of the covalent structure to the dative state. V is large for stable $n\nu$, $\pi\nu$, and $n\sigma$ complexes[35]. Owing to the presence of the contribution of V, the purely ionic triplet level of the dative structure

$$^3W_1 = I_D - E_A - Q - P + C + (V - K) \quad (10)$$

lies above the singlet level

$$^1W_1 = I_D - E_A - Q - P + C - (V - K). \quad (11)$$

for the majority of donor–acceptor systems.

The CTC triplet state (^3W, Fig. 1) arises after the complete electron transfer from the donor to the acceptor and constitutes none other than a purely ionic triplet configuration of the dative structure[33]. The wave function of the triplet state of the complex (φT) is described by a

combination of the wave functions $\varphi(D^{\ddagger})$ and $\varphi(A^{\bar{\cdot}})$ corresponding to the distribution of the unpaired electron densities in the radical-cation ($D^{\ddagger}$) and radical-anion ($A^{\bar{\cdot}}$):[33]

$$\begin{aligned}\varphi_T(m_s = +1) &= A\{\varphi(D^{\ddagger}\uparrow)\varphi(A^{\bar{\cdot}}\uparrow)\},\\ \varphi_T(m_s = -1) &= A\{\varphi(D^{\ddagger}\downarrow)\varphi(A^{\bar{\cdot}}\downarrow)\},\\ \varphi_T(m_s = 0) &= (\psi_I - \psi_{II})/(2 - S_{01}^2)^{1/2},\end{aligned} \tag{12}$$

where

$$\begin{aligned}\psi_I &= A\{\varphi(D^{\ddagger}\uparrow)\cdot\varphi(A^{\bar{\cdot}}\downarrow)\} \text{ and}\\ \psi_{II} &= A\{\varphi(D^{\ddagger}\downarrow)\cdot\varphi(A^{\bar{\cdot}}\uparrow)\}.\end{aligned} \tag{13}$$

The arrows indicate the direction of the spin of the unpaired electron.

In the presence of a contribution by V the ^3W level can lie above W_V for a weak CTC, which in the limit becomes a contact CTC (section II, Fig. 1) with $W_{01} \simeq 0$, $S_{01} \simeq 0$, and $W_V \simeq {}^1W_1$ [Eqn. (6)].[44-46] It shifts to the region $W_N < {}^3W < W_V$ on passing to a stable CTC (section I, Fig. 1) and, as the difference $I_D - E_A$ decreases, it falls to the level $J = {}^3W - {}^1W_1 = 2(V - K)$ on transition to radical-ion salts, for which $W_{01} = 0$, $S_{01} = 0$, and $W_N = {}^1W_1$ [Eqn. (5)].

In $\pi\pi$ complexes the V term is insignificant and the dative structure is largely ionic ($D^{\ddagger}A^{\bar{\cdot}}$). For such complexes, there is a possibility of a shift of the triplet level to a position below the singlet dative level [Eqns. (10) and (11)].[47,48]

As already mentioned, the dissociation of donor–acceptor complexes into radical-ions is the primary step of the complex process leading to a change in the absorption spectra of film materials. Since dissociation takes place with a greater probability after the light-induced population of the level with the most complete charge separation, it follows that the dissociative levels in weak, contact complexes are both the triplet level ^3W and the excited singlet level W_V, in a stable CTC only the ^3W level is dissociative, while in radical-ion salts both the triplet state and the ground singlet state are dissociative.

The dissociative level can be reached in contact complexes and CTC by the action of light corresponding to the absorption band of the complexes:

$$h\nu = W_v - W_N, \tag{14}$$

and in "reverse" CT by thermal excitation. Dissociation occurs when the dissociative level lies above the level of solvent-separated radical-ions ^2W,[49] i.e. under the condition

$$I_D - E_A - Q - \frac{2(\varepsilon - 1)}{2\varepsilon + 1}\cdot\frac{\mu^2}{a^3} \gtrless \gtrless I_D - E_A - Q_i - \frac{2e^2}{r_i}\left(1 - \frac{1}{\varepsilon}\right).$$

Here $[2(\epsilon - 1)/(2\epsilon + 1)](\mu^2/a^3)$ is the polarisation energy of the dipole $\mu = r_{D^{\ddagger},A^{\bar{\cdot}}}e'$,[37,40] $r_{D^{\ddagger},A^{\bar{\cdot}}}$ the distance between the donor and acceptor components of the complex, ϵ the dielectric constant of the medium, a the radius of the cavity polarised by the dipole μ, $(e^2/r_i)(1 - 1/\epsilon)$ the polarisation energy of the radical-ion with radius r_i, and Q_i the energy of the Coulombic attraction between the solvent-separated radical-ions.

The photodissociation process for the dissociative level ^3W is illustrated in Fig. 2. Many non-ordered systems incorporating CTC, liquids and films, are characterised by the presence of radical-ions even under conditions where the difference $^3W - W_N$ [see Eqns. (12), (13), and (2)–(5)] is fairly large and cannot ensure thermal dissociation. According to Stewart and coworkers[50,51], the appearance of radical-ions under dark conditions is associated with the formation of a CTC in an excited triplet state at the instant of formation of the complex on dissolution of an acceptor in a donor liquid. Then $^3W - W_N = \Delta H + \delta$, where $\Delta H = W_0' - W_N$ is the heat of formation of the complex and $\delta = {}^3W - W_0'$ the activation energy for the thermal formation of radical-ions.

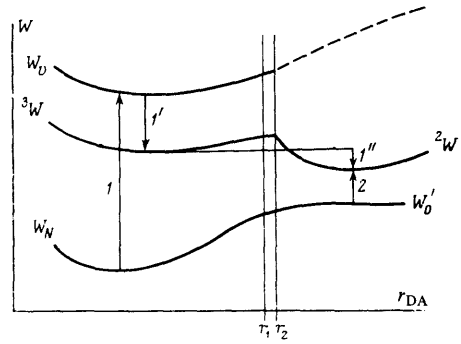


Figure 2. Schematic illustration of the formation of radical-ions in a non-ordered donor–acceptor system: 1),1'), and 1'') photodissociation of the CTC; 2) thermally excited D + A systems; W_0'—the level of separated D and A; ^2W the level of separated $D^{\ddagger}$ and $A^{\bar{\cdot}}$; $r_{DA} < r_1$—the CTC region; $r_1 < r_{DA} < r_2$—exciplexes; $r_{DA} < r_2$—separated D and A or $D^{\ddagger}$ and $A^{\bar{\cdot}}$.

The above explanation is apparently not the only one possible. As shown in Fig. 2, in a liquid and in films where both CTC and solvent-separated D and A exist simultaneously in equilibrium, one may expect the occurrence of reaction via pathway *2* on thermal excitation:

$$D + A \xrightarrow{\Delta E} D^{\ddagger} + A^{\bar{\cdot}}$$

without collision of the species. According to the theory developed by Dogonadze and Kuznetsov[52], reaction via pathway *2* takes place without change of the distance between the components and is due to a tunnel electron transfer. This transfer occurs on thermal excitation of the (D + A) system to the position coinciding with the ^2W level and under conditions where, in consequence of fluctuation-induced changes, the orientation of the solvent relative to the A and D molecules coincides with the orientation about the A^- and D^+ ions.

The photodissociation of CTC into radical-ions was first suggested by McGlynn and coworkers[45,46]. The photochemical decomposition of CTC has been examined in the reviews of Sergeev and coworkers[53,54], Nagakura[55], Davidson[37], and in a study by Irie et al.[58] on the use of this phenomenon in photopolymerisation, photosynthesis, and photochemical oxidation.

The elucidation of the nature of the dissociative level is important for finding the conditions under which light-sensitive systems operate. For dissociation via the triplet level in liquid and film systems, oxygen (the quenching agent for triplet energy) greatly reduces the quantum yield of the photodissociation products, which determines the light sensitivity of the system[13,55,59]; the

lack of an effect by molecular oxygen means that dissociation takes place via a singlet state, a characteristic solely of contact complexes[55,59,60-62].

Photodissociation can also occur via the excitation of both the complex and its individual components. In the latter case the electron transfer from the donor to the acceptor is due to the decrease of the difference $I_D - E_A$ owing to the decrease of I_D by $\sim h\nu_D$ on excitation by light corresponding to the absorption band of the donor or an increase of E_A by $h\nu_A$ when the system is acted upon by light corresponding to the absorption band of the acceptor[18,22,63]. The photoexcitation of an individual component is effective when the component of the complex whose colour changes is light-sensitive and the content of the second component, determined by the equilibrium constant

$$K = [DA]/[D][A], \quad (15)$$

ensures that a dominant proportion of the light-sensitive component exists in the form of the complex. The simultaneous presence of the light-sensitive component both as part of the complex and in the free state is responsible for the decrease of the quantum yield of the photodissociation products of the complexes (as a result of the absorption of part of the light quanta by the free molecules).

III. THE LIMITING LIGHT SENSITIVITY OF THE LAYERS IN THE ABSENCE OF IMAGE INTENSIFICATION

The principal characteristics of photolayers are light sensitivity and resolving capacity. Since in organic materials an individual molecule reacts, the resolving capacity of such materials is extremely high and their light sensitivity is low because it is limited by the quantum yield $\Phi \leq 1$. It is possible to estimate the upper limit to light sensitivity on the basis of the decrease of the concentration c of the component undergoing a colour change (or of the entire CTC):

$$-dc/dt = I_{abs}\,\Phi/l, \quad (16)$$

where I_{abs} is the power of the light flux absorbed by the film and l is the film thickness. After substituting $c = D/\epsilon l$ and $I_{abs} = I_0(1 - 10^{-D_1})$ in Eqn. (16), D being the optical density of the component whose colour changes, D_1 the optical density of the layer in the wavelength range of the incident light, ϵ the extinction coefficient, and I_0 the power of the light flux incident on the film, the relation between the incident energy of the light flux $I_0 dt$ ($J\ cm^2$) and the change in D assumes the following form:

$$I_0\,dt = \frac{dD}{1-10^{-D_1}}\,\frac{1.196\cdot 10^5}{\varepsilon\Phi\lambda}. \quad (17)$$

Here ϵ is expressed in litre^3 mole^{-1} cm^{-1} for a liquid and in dm^3 mole^{-1} cm^{-1} for films, λ being the wavelength of the incident light in nm. According to a USSR Government Standard (GOST), the light sensitivity of silver bromide layers is determined from the energy of the incident light causing a change in optical density by $\Delta D = 0.2$:

$$S_{0.2} = 10^{-4}/I_0\Delta t K,$$

where K is the coefficient of visibility with a maximum value of 680 at 555 nm.[64] Having adopted $\Phi = 1$, $\epsilon = 10^5$ dm^3 mole^{-1} cm^{-1}, $10^{-D_1} \ll 1$, and a wavelength of incident light $\lambda = 555$ nm identical with that corresponding to the absorption maximum of the compound, we find

$$I_0\Delta t_{0.2} \simeq 0.4\cdot 10^{-3}\ J\ cm^{-2},$$

i.e. the limiting attainable light sensitivity corresponds to $S_{0.2} \simeq 4\times 10^{-4}$ GOST units and is lower by several orders of magnitude than for silver bromide films. It is noteworthy that, in order to estimate the light sensitivity of non-silver layers, the value of $I_0\Delta t_1$ corresponding to a change of D by $\Delta D = 1$ was adopted. At the present time $I_0\Delta t_1$ is used mainly when information is recorded by decolorising coloured films, particularly for high optical densities. When a colour was imparted to colourless films, the light sensitivity was estimated in many investigations from $I_0\Delta t_{0.2}$.

Thus systems with $\Phi \leq 1$ can be used successfully in microfilming, where the resolving capacity of the layer is of decisive importance. The problem of obtaining layers with a high light sensitivity requires image intensification analogous to development in silver bromide photography and leading in its turn to a decrease of the resolving capacity, because a grain and not a molecule is now the light-sensitive element.

IV. LIGHT SENSITIVE CHARGE-TRANSFER COMPLEXES BASED ON ORGANIC SYSTEMS

Light-sensitive compositions, consisting of cyanine dyes[65] and their bases[66,67], leucoxanthenes, leucoanthraquinone, leucodiarylmethanes[66,68], amines[67,69,70], leucotriphenylmethane and styryl dyes[13-16,71,72] (as the donor component which undergoes a colour change), and the A–C–X$_3$ acceptors[13-16,65-72] (where A = H, Cl, Br, or I, and X = Cl, Br, or I) or $Cl_2BrCCBrCl_2$, as well as sulphur-containing acceptors of the type ArSh and ArS_2Ar or sulphophenyl halides[66], are being widely used nowadays and are being introduced into industry. In addition to the above substances, the compositions include also a free radical inhibitor and a polymeric binder. The light sensitive composition is deposited on either a paper or a polymeric support. It is noteworthy that the Horizons Co. Inc. in the USA alone took out more than 250 patents for light-sensitive compositions of this type.

Photochemical reactions in solid layers have been investigated in greatest detail using leucotriphenylmethane dyes[13-16] (DyeH) in combination with CBr_4, for example, leuco-Crystal Violet with added inhibitor of $CBr_2^{\cdot\cdot}$ (triphenylantimony) and a polystyrene binder. It has been shown[13-16] that, in contrast to DyeH and CBr_4, which absorb in the region below 370 nm, compositions with these substances give rise to an additional spectrum up to 450 nm, which imparts a yellow colour to the entire film. The additional absorption indicates the formation of a CTC (we shall designate it by DyeH.CBr$_4$). The photodissociation of the CTC on illumination by light corresponding to its absorption band [Eqns. (14)] takes place only in the absence of O_2 and therefore proceeds via the population of the triplet level ^3W in accordance with reaction

$$\begin{aligned} DyeH\cdot CBr_4 &\xrightarrow{h\nu_1} (DyeH\cdot CBr_4)^* \rightarrow {}^3(DyeH^+ + CBr_4^-), \\ {}^3(DyeH^+ CBr_4^-) &\rightarrow DyeH^+ + CBr_4^-. \end{aligned} \quad (18)$$

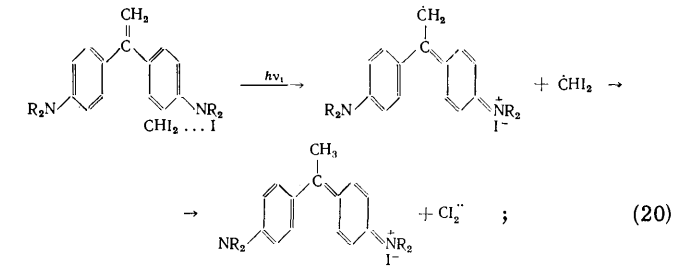
The dye responsible for the image (Dye$^+$), which absorbs in the visible region ($\lambda_{2,\max} = 600$ nm, $\epsilon = 1.2\times 10^5$ dm^3 mole^{-1} cm^{-1}), arises via the reaction

$$DyeH^+ + CBr_4^- \rightarrow Dye^+Br^- + HBr + CBr_2^{\cdot\cdot}. \quad (19)$$

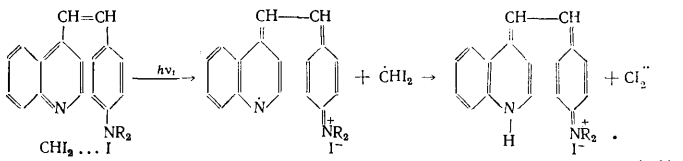
The $CBr_2^{\cdot\cdot}$ radicals which fog the film interact with the added inhibitor, restoring the transparency of the film.

The quantum yield at this stage, under the conditions of continuous circulation of gaseous nitrogen, is $\Phi = 0.1$ and corresponds to $I_0\Delta t_{0.2} = 10^{-2}$ J cm^{-2}.

The formation of an image in layers incorporating a CTC based on CHI_3 and vinylidene or substituted styryl components is due to an analogous set of reactions[71]. The absorption spectra of these compounds are displaced under illumination to a lesser extent than in the transition DyeH → Dye$^+$, since it does not entail an increase in the size of the continuous conjugation system [*Nl* in Eqn. (1)] and is due solely to the formation of electron-accepting groups via the following respective reactions:



(20)



(21)

The initial CTC absorb in these systems in the region of 488 nm and the resulting dyes absorb at λ_{max} = 620 and 580 nm respectively.

The problem of the optical development of the exposed film is also discussed in the studies quoted above[13-16,71]. The latent image arising as a result of brief exposure to radiation with $\lambda_1 < 450$ or 488 nm may be developed via reactions (18)–(21) by light corresponding to the absorption band of the dye. The dye molecules are then used as sensitisers. The effect is absent in the presence of O_2, which indicates energy transfer via triplet levels. The formation of a grain consisting of dye molecules during development takes place via the mechanism[13]

$$\mathrm{Dye}^+ \xrightarrow{h\nu_2} {}^1\mathrm{Dye}^{+\bullet},$$

$$^1\mathrm{DyeH}^{+\bullet} \rightarrow {}^3\mathrm{Dye}^+,$$

$$^3\mathrm{Dye}^+ + (\mathrm{DyeH}\cdot\mathrm{CBr}_4) \rightarrow \mathrm{Dye}^{\cdot+} + {}^3(\mathrm{DyeH}^+\cdot\mathrm{CBr}_4^{\cdot-}).$$

and then in accordance with reactions (18) and (19). Owing to the absence of inclusions of dye molecules at the unexposed sites, the film remains yellow after development due to the presence of the CTC. In contrast to the process discussed above, another mechanism, consisting in the thermal dissociation of the complex as a result of the liberation in a microvolume of the energy absorbed by the dye Dye$^+$ inclusions, has been suggested[14-16]. This conclusion is based on the fact that layers containing DyeH become coloured also on heating. The image is fixed by keeping the film at a temperature of ~140°C, which ensures the decomposition of the halogen-containing component and hence the decomposition of the CTC. The yellow colour then disappears and the unexposed sites become clear. It has been shown[13] that the image can be intensified in this way by a factor of ~1400, with an increase of the effective quantum yield to ~140 and of $I_0\Delta t_{0.2}$ to 7×10^{-6} J cm^{-2}. This corresponds to $S_{0.2}$ = 0.03 GOST units. In the best specimens $S_{0.2}$ reaches 0.1 (Fotland and Fichter[72]) and is close to the light sensitivity of silver halide films with a high resolution.

Polymeric films incorporating CTC comprising an amine (Am) (dibenzylaniline)[70,73,74] and CBr_4 are not coloured on heating to 250°C. Analysis of the influence of triplet energy acceptors on photochemical reactions[73] has established that the complex Am.CBr_4 (λ_{max} = 365 nm) does not dissociate on photoexcitation and, after an intercombination conversion, transfers to the triplet levels the energy absorbed by the Am molecules not involved in the CTC. At high concentrations of the added components, the latter form the exciplex ^{3}(Am).CBr_4, which dissociates via the mechanism

$$^3(\mathrm{Am})\cdot\mathrm{CBr}_4 \rightarrow (\mathrm{Am}^{+\bullet}\cdot\mathrm{Br}^- + \dot{\mathrm{C}}\mathrm{Br}_3) \rightarrow \mathrm{Am}_1^+\cdot\mathrm{Br}^- + \mathrm{HBr} + \ddot{\mathrm{C}}\mathrm{Br}_2 \quad (22)$$

with formation of Am_1^+ (C_6H_5–CH=$\overset{+}{N}$(–C_6H_5)–CH_2–C_6H_5), which absorbs in the visible region with λ_{max} = 665 nm. The optical intensification of the image in this system takes place via a two-quantum mechanism[74] in accordance with the relation (for Am ≫ Am_1^+)

$$\lg\frac{10^D-1}{10^{D_0}-1} = \frac{al_0^2}{bl_0+c[A_1]}\cdot\frac{[Am]}{d[A_2]+f[Am]+g}\cdot\frac{[CBr_4]}{k+h[CBr_4]}\cdot(t-t_0), \quad (23)$$

where D and D_0 are the optical densities at 665 nm at times t and t_0, a, b, c, d, f, g, h, and k are constant coefficients, A_1 and A_2 are oxygen or other acceptors of the triplet energy of singly and doubly excited Am_1^+ species respectively, and I_0 is the intensity of the light acting in the region of λ = 665 nm.

Optical intensification made it possible to increase the effective quantum yield from ~0.14 to ~14 and the light sensitivity at 365 nm from 1.4×10^{-2} to 1.4×10^{-4} J cm^{-2}. In contrast to layers based on leucodyes, amine-containing films are more stable and do not lose their light sensitivity for a long time. In the fixation of films by heating, a stable dye is synthesised simultaneously from Am_1^+ and other components of the layer.

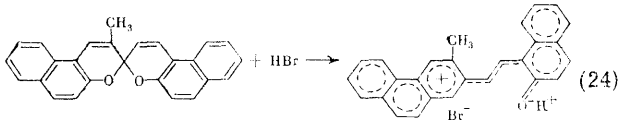
In a photoreproduction process, amines such as *N*,*N*′-diphenylenediamine, *N*,*N*′-diphenyl-*p*-phenylenediamine, and others are used in combination with CBr_4 [75] or CHI_3.[76] These systems are also sensitive to ultraviolet light and the appearance of a colour in them is associated with the formation of stable radical-cations.

The region of spectral sensitivity of the films has been extended to ~540 nm when the bases of cyanine dyes began to be used in conjunction with CBr_4 [66,67] and to 700 nm when cationic cyanine dyes were used[65]. The presence of CTC of CBr_4 and cyanine dyes or their bases has been merely postulated[65,67]. These systems are used without image intensification. Compositions consisting of cationic cyanine dyes and anionic aryl borates $(BR_1R_2R_3R_4)^-$, where R_{1-4} are aryl-substituted groups which are effectively decolorised on photoexcitation of the dye, have also been proposed for use in reproduction using visible light. Lifanov et al.[77] and Chibisov[78] established that, on photoexcitation of cyanine dyes, there is an effective electron transfer to the dye with formation of a radical-anion if the system contains simultaneously a donor (ascorbic acid, diphenylamine, hydroquinone, etc.), but in the presence of acceptors the products are radical-cations.

The photographic process involving A–C–X_3 is referred to by convention as a free radical process. It is noteworthy that in all systems free-radical reactions take place under the conditions of the photoexcitation of the halogenomethane (<300 nm) as a result of its dissociation, for example into CBr_3 and Br$^\cdot$, and the occurrence of subsequent reactions with participation of these radicals[69]. When the reactions are initiated by the photoexcitation of

the CTC or the donor under these conditions, the primary stage is electron transfer from the donor to the halogenomethane. This transition has been demonstrated by flash photolysis[18,79] using also the aromatic amine–CCl_4 liquid system. The nature of the subsequent reactions is determined by that of the donor. In contrast to the compositions examined above, these reactions take place with participation of the $\dot{C}Br_3$ radical also in the liquid phase via a chain mechanism when donors such as diphenylamine[69] and polyvinylcarbazole (PVCA) are used[80]. When illuminated films containing PVCA and halogenomethane complexes are placed in a solvent, the effective quantum yield of the PVCA photochemical oxidation product increases from 5×10^{-2} to approximately unity as a result of the decrease of the rigidity of the matrix and the establishment of conditions for the occurrence of free-radical reactions[80].

Smets et al.[81] proposed a complex light-sensitive system incorporating the CTC of polyvinylcarbazole and CBr_4 as well as di-β-naphthospiropyran. The well known[2,5] displacement of the absorption spectra of spiropyrans from the ultraviolet to the visible region under dark conditions when the pH changes as a result of the occurrence of the reaction


(24)

is used in this system. The enhancement of the acid properties of the films is due to the photodissociation of the CTC on exposure to light corresponding to its absorption band [Eqn.(14)] at $\lambda_1 = 405$ nm: $PVCA.CBr_4 \xrightarrow{h\nu_1} (PVCA.CBr_4)^*$ and then

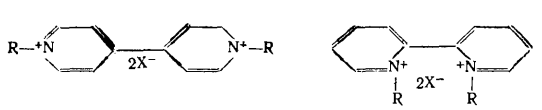
$$(PVCA\cdot CBr_4)^* \rightarrow PVCA^{\ddagger} + HBr + \dot{C}Br_3. \qquad (25)$$

The quantum yield of the products of reaction (25) is close to 0.23 and is independent of the CBr_4 content. The authors demonstrated the possibility of the optical manifestation of the latent image produced on exposure by employing as sensitiser di-β-naphthopyrylium bromide (DNP), formed by reaction (24) and absorbing in the range $\lambda_2 = 600$–700 nm. Since the rate of development increased in proportion to the CBr_4 concentration, the authors postulated the formation of CTC between DNP and CBr_4 and their participation in the development reaction:

$$DNP\cdot CBr_4 \xrightarrow{h\nu_2} (DNP\cdot CBr_4)^*,$$
$$(DNP\cdot CBr_4)^* + PVCA\,CBr_4 \rightarrow DNP\cdot CBr_4 + (PVCA\cdot CBr_4)^*,$$

this being followed by reaction (25). The HBr formed by reaction (25) ensures the appearance of an additional amount of coloured DNP by reaction (24). It was also established that the $\dot{C}Br_3$ radicals are inserted in the chain and that, together with $PVCA^{\ddagger}$, they ensure the cross-linking of the polymer in the exposed regions. In this system there is a possibility of the appearance of an image as a result of the dissolution of the non-cross-linked PVCA.

Systems based on bipyridylium salts with acceptor properties, such as 2,2′-bipyridylium (2,2′-$BP^{2+}2X^-$) and 4,4′-bipyridylium (4,4′-$BP^{2+}X^-$) also acquire a colour on ultraviolet irradiation:



They exist either in low-molecular-weight[82–85] or polymeric forms[86]. The optical absorption spectra of the above dications lie in the range 200–300 nm. Photoexcitation of the salt in the presence of a donor component such as the film-forming poly(vinyl alcohol)(PVA) [82–85] leads to the formation of the radical-cations $BP^{\ddagger}$ via the mechanism (in relation to the 4,4′-BP^{2+}–PVA system):

$$BP^{2+} \xrightarrow{h\nu_1} (BP^{2+})^* \xrightarrow{RCH_2OH} BP^{\ddagger} + H^+ + R\dot{C}HOH,$$
$$BP^{2+} + R\dot{C}HOH \rightarrow RCHO + H^+. \qquad (26)$$

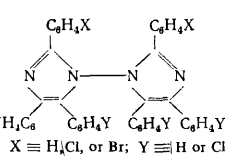
It has been established for aqueous solutions of BP^{2+} [87] that the photochemical reduction is irreversible only in the presence of primary and secondary alcohols, owing to the possible elimination of a proton in the α-position relative to the alcoholic group and the formation of the corresponding carbinol. The finding that the alcohols quench the fluorescence of 2,2′-BP^{2+} salts served as a basis for the conclusion that the electron-accepting state is the excited singlet state of the salt. It has been shown for the liquid phase[88–90] that 4,4′-BP^{2+} forms CTC with benzilate and oxalate anions, which absorb in the region of $\lambda_{max} =$ 370 nm and dissociate on photoexcitation with formation of $BP^{\ddagger}$. In a solid-phase system with 4,4′-$BP^{2+}X^-$ and PVA the quantum yield of the formation of the radical-cations depends on the nature of X^-. The values of $I_0\Delta t_{0.2}$, characterising the sensitivity of the films to light with $\lambda_1 =$ 270 nm, and the quantum yields Φ are listed below as a function of the anion in bipyridylium salts:

Anion	Br^-	SO_4^{2-}	NO_3^-	Cl^-
Φ	0.015	0.028	0.045	0.047
$I_0\cdot\Delta t_{0.2}\cdot10^3$, J cm^{-2}	200	130	82	80.6

The radical-cations $BP^{\ddagger}$ transfer their charge to oxygen when the latter is introduced. However, the solubility of oxygen in PVA films is so low that the image obtained persisted throughout the period of the observation (1 year). It has been suggested in a patent[85] that cationic dyes be introduced into a chloride–4,4′-bipyridylium–PVA composition. Heat treatment of this system after the photochemical reduction of the salt ensures the transfer of an electron from the radical-cation $BP^{\ddagger}$ to the dye and the decolorisation of the latter as a result of the formation of the leuco-form. Such electron transfer ensures an increase of photosensitivity within the limits of one order of magnitude owing to the increase of the extinction coefficient of the films from $(1.2$–$2.4)\times10^4$ dm^3 mole^{-1} cm^{-1} for $BP^{\ddagger}$ to $(0.8$–$1.2)\times10^5$ dm^3 mole^{-1} cm^{-1} on passing to the dye.

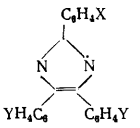
A composition of benzoyl-leuco-Methylene Blue as the donor and an aromatic nitro-compound as a photosensitive acceptor has also been proposed[91] as a system sensitive to ultraviolet light. Illumination of the system in a polymeric polyester binder for 2 s with light from a 20 W lamp and subsequent heat treatment at 120 °C for 5 s ensure the conversion of most of the leuco-form into the dye.

The du Pont de Nemours Co. (USA) developed a "dyelux" process[91–94], where the colour change is associated with the interaction of two basic components. Hexa-arylbisimidazoles having the structure


(27)

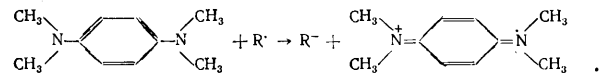
are used as the light sensitive component in this process. The component whose colour changes consists of amines[92,93] and leucodyes DyeH (see, for example, Ref. 94).

Under the influence of light with $\lambda_1 \simeq 250-360$ nm, the dimers (27) undergo homolytic dissociation with formation of the triarylimidazolyl radicals R$^{\cdot}$:[95]



(28)

These radicals absorb in the visible region (530–620 nm), but are characterised by a lower extinction coefficient [$\epsilon \simeq (1.3 - 8.1) \times 10^3$ litre mole^{-1} cm^{-1} in solution]. A detailed study of the nature of the reactions occurring in solution[1,2,96-100] showed that the radicals (28) oxidise amines in the dark[92,93,96] as well as leuco-dyes[94,96-100]. When amines are used, the appearance of the colour is due to the formation of radical-cations, for example by the following reaction in the case of tetramethyl-*p*-phenylenediamine[93,95]:



The resulting radical-cation has absorption maxima at 575 and 625 nm and the extinction coefficient in the film is $\epsilon \simeq 10^5$ dm^3 mole^{-1} cm^{-1}.

When the leuco-form of the dye is used, the colour is associated with the formation of the dye itself[94] by the reaction[96-100]

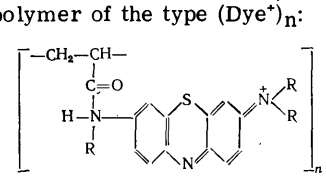
$$\mathrm{DyeH} + 2\mathrm{R}^{\cdot} \rightarrow \mathrm{Dye}^{+} + \mathrm{RH} + \mathrm{R}^{-}.$$

In order to rule out the acquisition of a colour by the unexposed regions of the film under the influence of ultraviolet light after the recording of the image, it has been suggested that a third component be used[94]—1,6- or 1,8-pyrenequinone or 9,10-anthraquinone—in combination with a polymeric donor matrix. As a result of the interaction with the matrix in an excited state (under the influence of light with $\lambda_2 = 380-500$ nm), the quinones (O=Ar=O) are converted into hydroquinones (HO–Ar–OH), which react with the dimers under dark conditions:

$$\mathrm{HO—Ar—OH} + \mathrm{R—R} \rightarrow \mathrm{O{=}Ar{=}O} + 2\mathrm{RH}.$$

ensuring the transformation of the dimer R–R (27) into the lophine form (RH), which is insensitive to the action of light with $\lambda > 250$ nm. The "dyelux" process does not provide for image intensification and can be used in the formation of duplicates in microfilming. Its sensitivity is $I_0 \Delta t_{0.2} = 2 \times 10^{-3}$ J cm^{-2}.

In order to obtain non-silver layers sensitive in the red part of the spectrum, Oster and coworkers[101-103] investigated the photochemical reduction of thiazine dyes, which have an optical absorption maximum at 590–665 nm, to the leuco-form, which absorbs in the ultraviolet when present in PVA films and in hydroxylated glasses—fructose, glucose, etc. In order to obtain films whose colour changes under the influence of red light, Kamogawa[104,105] synthesised a polymer of the type $(\mathrm{Dye}^{+})_n$:



(29)

The reduction of Methylene Blue (a thiazine dye) MB^{+} ($\lambda_{max} = 665$ nm) to the leuco-form MBH ($\lambda_{max} \simeq 260$ nm) in layers deposited on a support, under dark conditions on contact with gaseous H_2S as a donor, has been studied by Vartanyan[106,107], who suggested[106] that the photodecolorisation of MB^{+} in gelatine films observed by Lazarev (1912) is associated with the photochemical reduction of the dye to MBH. Oster et al.[101] showed that the rate of decrease of the optical density of the dye in hydroxylated films and glasses is accelerated after the introduction of electron-donating components such as ascorbic acid, phenylhydrazine, allylthiourea, $SnCl_2$, ethylenediaminetetra-acetic acid, etc., increasing linearly with increase of the ratio $(T/\eta)^{1/2}$, where T is the temperature and η the viscosity of the medium. This relation served as a basis for the conclusion that the decolorisation process is controlled by the diffusion of the components. It has been suggested that, in the absence of donors, the unexcited dye molecules serve as a reductant to a greater extent than the medium.

Kamogawa[104,105] investigated the photodecolorisation of polymeric dyes introduced into a PVA or cellulose matrix together with Fe^{2+} as the donor and enzymes. As expected from the consideration of the phenomenon in the liquid phase[108-111], the added Fe^{2+} ions do not ensure the complete decolorisation of the film, since the Fe^{3+} ions formed in the course of the reduction of the dye are a powerful oxidant and induce the reverse reaction in the dark. Enzymes increase the rate of the photochemical reduction of the polymeric dye, but the addition of water constitutes the most effective means of accelerating the photochemical decolorisation process. An estimate based on the experimental data presented in the relevant paper shows that the transmittance at $\lambda = 600$ nm increases from 4 to 94% as a result of the absorption of the light energy $I_0 \Delta t = 1-4$ J cm^{-2}.

The finding that the rate of photochemical reduction is controlled by diffusion and therefore proceeds slowly in the solid phase apparently limited the number of studies whose aim was to employ the photodecolorisation of thiazine dyes in photography. In contrast to solid layers, numerous studies have been devoted to the photochemical reduction of thiazine dyes in the liquid phase. When aqueous and alcoholic solutions are used, the nature of the decrease of the concentration of the dye following its photoexcitation confirms[112-116] the hypothesis but forward for the solid phase that the colourless leuco-form is produced as a result of the interaction of the excited dye molecule with a donor and, in its absence, with an unexcited dye molecule. A slow decomposition of the functional groups as a result of the interaction of the excited dye with the solvent has also been observed in alcoholic solutions. In aqueous and alcoholic solutions Dye^{+} and D do not exist as a complex but interact on collision, as shown by the increase of the quantum yield with increasing donor concentration in accordance with the relation

$$1/\Phi = a + b/[\mathrm{D}]. \qquad (30)$$

Arvan and coworkers[24,117-120] demonstrated the formation of a σ-complex (quasi-leuco-form) between Dye^{+} and the leuco-form of a dye of a different class and also between Dye^{+} and the solvent (pyridine) under the influence of light corresponding to the Dye^{+} absorption band. It was shown[120] that pyridine or an electron-donating additive add to the central nitrogen atom of the dye, which ensures its decolorisation. The increase almost by an order of magnitude of the rate of reduction of MB^{+} by hydrogenated aromatic hydrocarbons under dark conditions after the introduction of amines has been explained[121] by the primary formation of a σ-complex and its subsequent reaction with the hydrocarbons, terminating in the formation of MBH, the initial amine, and an aromatic molecule. In contrast

to PVA films, when poly(vinyl chloride) (PVC) was used as the film-forming material, the independence of the quantum yield of the products of the decolorisation of MB^+, in the presence of tribenzylamine (TBA) as the donor, of the MB^+ and TBA concentrations[122,123] was demonstrated for [TBA] > 0.1 mole dm^{-3}. The yield Φ was calculated from experimental data by the formula

$$\lg(10^{D_0}-1)-\lg(10^{D}-1)=\Phi\frac{\varepsilon\lambda I_0}{1.196\times10^6}\cdot\Delta t, \qquad (31)$$

obtained by integrating Eqn. (17) for $D = D_1$ and amounted to $\Phi = 0.08$. Here D_0 and D are respectively the optical densities (at $\lambda_{max} = 665$ nm) of the initial film and the film illuminated during the period Δt with monochromatic light ($\lambda = 652$ nm) having an intensity I_0.

The independence of Φ of [TBA] and [MB^+] indicates the presence of associated species comprising MB^+ and TBA, for example of the type of weak σ-complexes. The following set of reactions then take place:

$$(MB^+ \ldots TBA) \xrightarrow{h\nu_1} (MB^{+*} \ldots TBA),$$

$$(MB^{+*} \ldots TBA) \xrightarrow{k_1} (MB^+ \ldots TBA),$$

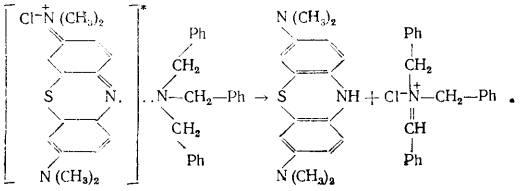
$$(MB^{+*} \ldots TBA) \xrightarrow{k_2} MBH + A_1^+,$$

and Φ is determined by the relation

$$\Phi = \frac{[MBH]}{[MB^{+*} \ldots TBA]} = \frac{k_2}{k_2+k_1},$$

which differs from Eqn. (30) for photochemical reduction on collision between the component molecules.

Since the rate of photodecolorisation of coloured PVC films on photoexcitation of MB^+ in the absence of a donor was the same as that measured in the presence of triphenylamine (TPA) but increased by a factor of 130 on passing to TBA and since the radicals MB· arose in the presence of TPA at higher concentration than after the addition of TBA, it was concluded that TBA ensures the reduction of MB^+ to MBH by transferring not only an electron but also a hydrogen atom to the dye via the reaction



At low TBA concentrations, corresponding to an appreciable fraction of MB^+ in a non-associated state according to Eqn. (15), the relation $\lg(10^D - 1) = f(\Delta t)$ gives rise to two sections corresponding to the photochemical reduction of the dye molecules in both associated and free states. The separation of these contributions at different TBA concentrations made it possible to determine $K \simeq 10$ dm^3 $mole^{-1}$ [Eqn. (15)]. In the system considered the light sensitivity in the region of $\lambda \simeq 600$–700 nm corresponds to a decrease of the optical density by $\Delta D = 1$ as a result of the effect of the incident light having an energy $I_0\Delta t_{1.0} = 33\times10^{-3}$ J cm^{-2}.[122,123] This quantity exceeds approximately by two orders of magnitude the light sensitivity of PVA films coloured by MB^+ and is due to the presence of associated species, which rule out diffusion-dependent limitation of the rate of the photochemical reaction.

Japanese investigators[1,31] suggested that dye layers vacuum sputtered onto a support at 60–70°C be used in reproduction (they designated these dyes by the abbreviation TED–Thermally Evaporated Dyes). The process is based on the ability of certain dyes to dimerise as a result of photoexcitation[18]. Since the dimers absorb light in the region displaced by several tens of nm towards shorter wavelengths compared with the absorption of the monomer, the image remains coloured and is difficult to distinguish from the unexposed regions. The image is developed by treating the layer with a non-polar solvent and heating. In the former case the dye is removed from the unexposed regions but remains in the exposed regions owing to the decrease of solubility as a result of the formation of dimers. In the case of xanthene dyes such as rhodamine B and its derivatives, the greater thermal stability of the dimers compared with the monomers is used. In order to develop the exposed regions, which have a higher content of dimers, use was made[31] of the ability of these dyes to undergo an irreversible conversion into the lactone form as a result of heating to 70–140°C, which has been thoroughly investigated[24,27,30]. After heating, the coloured layer remains on the exposed regions, but the unexposed regions become colourless, since, in contrast to the cationic dye which absorbs in the region of 550 nm, the absorption spectrum of the lactone form is in the ultraviolet. The light sensitivity of the layers is low (~0.3 J cm^{-2}), but the layers consist of only one component and are distinguished by a high resolving capacity.

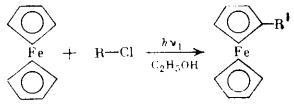
V. LIGHT SENSITIVE CHARGE-TRANSFER COMPLEXES BASED ON ORGANOMETALLIC COMPOUNDS

There exists yet another class of compounds which undergo further chemical reactions involving charge-transfer states and are extremely promising for the formation of image recording systems. These are organometallic compounds and in the first place ferrocene and its derivatives.

The fundamental studies carried out during the last ten years showed that the photochemistry of organometallic compounds has its characteristic features and many phenomena have still not been fully explained even for the simplest systems. Photochemical reactions involving the decomposition of many ferrocene derivatives were first observed by Nesmeyanov and coworkers[124–126]. A number of reviews have been devoted to the chemistry of metallocenes and transition metal carbonyls[127–129]. The mechanisms of photochemical reactions have been considered mainly in relation to solutions and it is very difficult to use these results for reactions in solid matrices, particularly since the solvent effects for organometallic compounds are very considerable. The use of organometallic compounds in recording systems is based on photochemical reactions in the solid state and, with a rare exception[130], the chemistry of photochemical processes has not been established at all reliably in most instances.

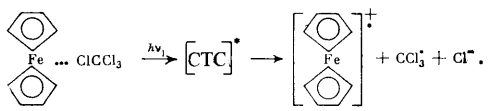
Systems where the photochemical reactions proceed with precipitation of charge-transfer complexes are of interest for the present review. These are the most promising for use in recording systems. Brand and Snedden[131] observed a dissociative charge-transfer band in the absorption spectra of ferrocene solutions in carbon tetrachloride. When these solutions are irradiated with ultraviolet light, ferricenium tetrachloroferrate(III) is formed quantitatively. In the presence of compounds containing mobile hydrogen, the ferricinium salt is transformed into ferrocene[132]. The formation of ferricinium

tetrachloroferrate(III) was also observed[133] in the photolysis of ferrocene in hexachlorocyclopentadiene. In solutions of organic halogeno-derivatives in ethanol photochemical substitution of ferrocene takes place[134]. It is thus possible to introduce ethoxycarbonyl, formyl, ethoxymethyl, benzyl, and allyl groups into the ferrocene molecule under the influence of ultraviolet light[135] via the general mechanism

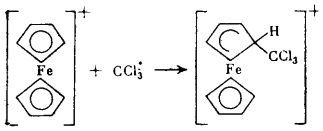


R = CCl_3, $CHCl_2$, or CH_2Cl;
R' = $CO_2C_2H_5$, CHO, or $CH_2OC_2H_5$.

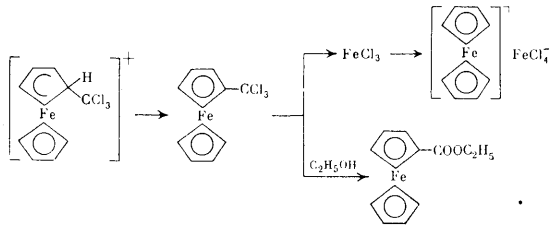
The ultraviolet absorption spectrum of ferrocene in ethanol has a band with λ_{max} = 440 nm, which has been attributed to a $d \rightarrow d^*$ transition and a band with λ_{max} = 325 nm assigned to $3d \rightarrow$ MO*, MO $\rightarrow$ MO*, or symmetry-prohibited $\pi \rightarrow \pi^*$ transitions. The absorption at wavelengths below 300 nm is apparently due to a $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition[136]. An absorption with a maximum at 307 nm, associated with charge-transfer, is manifested in ferrocene solutions in carbon tetrachloride. When other halogen-containing organic solvents are used, such as chloroform, dichloromethane, allyl bromide, benzyl chloride, trichloromethylbenzene, and *p*-nitrobenzyl chloride, λ_{max} for the charge-transfer band is located in the region between 300 and 380 nm, while for chlorides such as n-butyl chloride, allyl chloride, and a number of others, a charge-transfer band was not observed in the presence of ferrocene. Accordingly the yield of substitution products in the latter case is much lower than in systems forming CTC. The mechanism of the substitution reaction has been investigated in detail[137]. The dependence of the quantum yield of the photosubstitution reaction (and of the decomposition of ferrocene) on the wavelength shows that it is zero in the region of the $d \rightarrow d^*$ transition, while excited states with charge transfer lead to the effective formation of substitution products. Excitation by light at shorter wavelengths stimulates such reactions as a result of the decomposition of ferrocene molecules by the chlorine atoms generated by the direct photochemical decomposition of the halogenohydrocarbons. Measurements by flash photolysis[137] suggested a mechanism of the formation of coloured products: the first stage of the photochemical reaction is believed[131] to consist of the excitation and decomposition of the CTC:



According to Beckwith and Leydon[138], the ferricinium cation is extremely reactive towards free radicals, in contrast to ferrocene itself:



The subsequent stages were determined less reliably. On pulsed illumination, $FeCl_3$ is formed in an overall process which obeys first-order kinetics and has a rate constant of $\sim(1.6 \pm 0.5) \times 10^5$ s with subsequent formation of ferricinium tetrachloroferrate(III) and, in the presence of ethanol, of ferrocenecarboxylic acid:

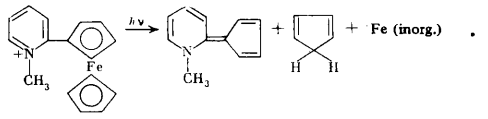


In contrast to normal ferricinium ions, ferricinium tetrachloroferrate(III) does not interact with trichloromethyl radicals. It has been suggested that the formation of ferricinium tetrachloroferrate(III) in ferrocene solutions in CCl_4 be used in ^{60}Co γ-radiation dosimeters[139], because the concentration of the ferricinium salt formed is proportional to the absorbed dose.

The formation of CTC between ferrocene and halogenohydrocarbons is used in recording layers. On formation of the CTC in the solid state, the acceptor interacts with the pentadienyl ring and not with the metal[134]. The exact mechanism of the photochemical processes in such solid systems has not been investigated, but there is no doubt that its main stages have much in common with reactions in solution. Compositions containing ferrocene or its derivatives and photolytic halogenohydrocarbons are characterised by a spectral sensitivity which embraces the visible region, in contrast to many other organic systems which are sensitive only in the ultraviolet region. In a system incorporating ferrocene and CBr_4 a complex having the composition Fc.3CBr_4 with λ_{max} = 388 nm is formed[143]. The absorption band of the complex extends into the visible region up to ~600 nm. The bathochromic shift of the CTC absorption band when CCl_4 is replaced by CBr_4 is associated with the increase of the electron affinity (0.15 and 1.17 eV respectively). The formation of the CTC and its absorption spectrum fully determine the light sensitivity of the recording layers and its spectral range[143].

Compositions based on ferrocene or its derivatives and halogenohydrocarbons are used in the manufacture of reproducing materials with an increased sensitivity in the visible light. These layers can be effectively stored in the dark, are fixed on heating, are readily activated, and do not require a chemical treatment[140]. Other ways of employing light-sensitive layers containing CTC have also been proposed. Thus layers based on vinylferrocene copolymers with halogenohydrocarbons become electrically conducting in the exposed regions. The subsequent employment of electrophotographic stages makes it possible to obtain a large number of copies from a single exposed layer. Layers with CTC comprising vinylferrocene copolymers with nitrogen-containing heterocyclic compounds and halogenohydrocarbons have now been obtained; after their exposure and treatment with methanol, a coloured image is produced[141].

The latter process can also be regarded as a photochemical reaction of the ammonium forms of nitrogen-containing ferrocenes[142], which was first observed in relation to α-ferrocenylpyridinium methiodide:



The above discussion shows that definite achievements have been made in the use of charge-transfer states for the formation of light-sensitive layers with a wide variety of photographic characteristics. Interactions with charge transfer are universal—it is difficult to point to a system in which they do not occur and in which they do not contribute to photochemical processes, but their detection involves difficulties in many instances. The formation on photoexcitation of radical-cations and radical-anions changes the spectroscopic characteristics in the visible region under the influence of infrared and ultraviolet radiation, which makes it possible to obtain contrasting layers. One may also note that, among other organic systems, only layers based on the use of charge-transfer states approach the sensitivity of silver bromide layers. This is associated with the possibility of using physical developers and of intensifying the latent image by the action of light corresponding to the absorption band of the coloured photochemical reaction products. These layers also possess special properties—sensitivity within narrow spectral regions of the visible, infrared, and ultraviolet, the possibility of multicoloured recording, as well as the recording of holograms.

The mechanism of the photochemical reactions of CTC has been studied mainly in solution. The application of the results to solid layers is open to serious objections, particularly in systems sensitive to the characteristics of the medium. The study of the photochemistry of charge-transfer states in solid multicomponent systems forming CTC is therefore important for the development of light-sensitive layers.

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The Insertion of Diene Hydrocarbons in a Transition Metal - Ligand Bond

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Reactions involving the insertion of diene hydrocarbons in transition metal - ligand bonds, leading to the formation of σ- or π-allyl complexes, are examined and their possible mechanisms are discussed.
The bibliography includes 242 references.

CONTENTS

I.	Introduction	758
II.	Insertion in transition metal - hydrogen bonds	758
III.	Insertion in transition metal - carbon σ-bonds	762
IV.	Addition of dienes to π-allyl metal - carbon bonds	763
V.	Insertion of dienes in transition metal - acido-ligand bonds	765
VI.	The mechanism of stereoregulation in reactions involving the insertion of dienes in transition metal - ligand bonds	767

I. INTRODUCTION

Progress in polymerisation catalysis achieved in recent years has been largely due to the involvement of organometallic compounds in research. The use of catalytic systems based on aluminium and transition metal compounds made it possible to carry out specific syntheses of many olefin and diene polymers and to organise the industrial production of polyethylene, polypropylene, and stereoregular rubbers, including isoprene rubber.

Among many pathways leading to the reaction of unsaturated hydrocarbons under the influence of organometallic compounds, the addition of the latter to multiple carbon–carbon bonds is of particular interest. Active metal–carbon bonds, capable of involvement in further chemical reactions, persist in the resulting adducts. Numerous repetition of the addition steps, achieved in many instances, leads to the formation of long hydrocarbon chains, i.e. telomer or polymer molecules.

Studies on the addition of organic derivatives of metals to conjugated multiple carbon–carbon bond systems have yielded extremely valuable information for the development of organometallic and organic chemistry. The wide variability of the structures of the adducts formed and their dependence on the nature of the reactants made it possible to outline various approaches to the study of the mechanisms of the reactions of unsaturated compounds.

In contrast to the addition of organometallic compounds to mono-olefins, in the case of conjugated diene systems adducts are formed with a metal atom in the β-position relative to the double bond. When there are coordination vacancies in the metal, such σ-compounds can be converted into thermodynamically more favourable π-allyl complexes in which the bond with the metal is formed with participation of three carbon atoms. In the presence of substituents at the terminal carbon atoms of the π-allyl group, the "non-classical" structure of the π-allyl complexes is responsible for the non-equivalence of the bonds of the metal with the first and third carbon atoms and also for the existence of complexes in two isomeric forms (*syn*- and *anti*-). All these facts must be taken into account in determining the mode of addition of transition metal derivatives to diene hydrocarbons.

The synthesis of diene polymers under the influence of metal complex catalysts is carried out by inserting the monomer molecules in metal–carbon bonds. The study of the simplest reactions of this type is therefore of undoubted interest for the development of ideas concerning the mechanisms of the elementary stages in the polymerisation of diene hydrocarbons, which are practically important processes.

An attempt was made in the present review to survey all the available experimental data on the reactions involving the insertion of diene hydrocarbons in active metal–ligand (hydride, alkyl, acyl, allyl, and acido-groups), which can be regarded as model reactions leading to the formation of active centres in various organic synthetic and polymerisation processes with participation of diene hydrocarbons. The insertion of dienes in metal–ligand bonds is also used widely as one of the preparative procedures for the synthesis of allyl complexes of transition metals[1,2].

II. INSERTION IN TRANSITION METAL–HYDROGEN BONDS

1. Buta-1,3-diene

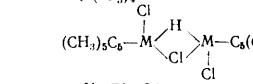
Transition metal hydrides add to butadiene with formation of both σ- and π-crotyl 1 : 1 adducts, the insertion in the latter case being accompanied by the displacement of one monodentate ligand from the coordination sphere of the metal.

At moderate temperatures hydridopentacarbonylmanganese adds to butadiene in the 1,4-positions[3,4]. The reaction products contain 85% of the *cis*-σ-crotyl complex and 15% of the *trans*-isomer. Hydridocyclopentadienyldicarbonyliron reacts similarly under these conditions[5]. At 80–100°C in the former case and under ultraviolet irradiation in the latter, mainly *syn*-π-crotyl complexes are formed. Mild decarbonylation and a mixture of *cis*- and *trans*-σ-crotylmanganese pentacarbonyls with the aid of bis(diphenylphosphinoethane)iridium chloride takes place with retention of the geometrical configuration of the crotyl ligand[6].

The π-crotyl structure has been established for butadiene adducts and all the remaining hydrides listed in Table 1. It is therefore impossible to determine the mode of addition (in the 1,2- and 1,4-positions). Table 2 presents the known examples of reactions involving the

insertion of butadiene in transition metal–hydrogen bonds formed when compounds of these metals are reduced in the presence of butadiene.

Table 1. The insertion of butadiene in transition metal–hydrogen bonds.

Initial compound	Reaction product	References
$HMn(CO)_5$	*cis-* and *trans-* $CH_3CH{=}CHCH_2{-}Mn(CO)_5$	3
$HFe(C_5H_5)(CO)_2$	*cis-* and *trans-* $CH_3CH{=}CHCH_2{-}Fe(C_5H_5)(CO)_2$	5
$HFe(NO)(CO)_3$	$C_4H_7Fe(NO)(CO)_3$	7,8
$HFe(CO)_4SiCl_3$	*anti-* $C_4H_7Fe(CO)_3SiCl_3$	9
$HCo(CO)_4$	*syn-* and *anti-* $C_4H_7Co(CO)_3$	3,10–13
$HCo(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_n$ ($n = 2,3$)	$C_4H_7Co(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_{n-1}$	14
$HCo(N_2)[P(C_6H_5)_3]_3$	*syn-* $C_4H_7Co(C_4H_6)P(C_6H_5)_3$	15
$HCo(PF_3)[P(C_6H_5)_3]_3$	*anti-* $C_4H_7Co(C_4H_6)PF_3$	16
$[HNi[P(OCH_3)_3]_4]^+HSO_4^-$	*syn-* and *anti-* $[C_4H_7Ni[P(OCH_3)_3]_3]^+HSO_4^-$	17,18
$[HTi(C_6H_5)_2]_2$	$C_4H_7Ti(C_6H_5)_2$	19,20
$HV(CO)_6$	*syn-* and *anti-* $C_4H_7V(CO)_5$	21,22
$HRh(CO)[P(C_6H_5)_3]_3$	$C_4H_7Rh(CO)[P(C_6H_5)_3]_2$	23
$HRh[P(C_6H_5)_3]_4$	*syn-* and *anti-* $C_4H_7Rh[P(C_6H_5)_3]_2$	24
$HRh(PF_3)_4$	*syn-* and *anti-* $C_4H_7Rh(PF_3)_3$	25,26
	*syn-* $C_4H_7M(Cl)[C_5(CH_3)_5]$	27–29
($M = Rh, Ir$)		
$[HIr[C_5(CH_3)_5]X]_2$ ($X = Cl, Br, I$)	*syn-* $C_4H_7Ir(X)[C_5(CH_3)_5]$	30
$HIr(CO)_2[P(C_6H_5)_3]_2$	$C_4H_7Ir(CO)[P(C_6H_5)_3]_2$	23
$HPt(NO_3)[P(C_2H_5)_3]_2 + NaB(C_6H_5)_4$	$[C_4H_7Pt[P(C_2H_5)_3]_2]^+B(C_6H_5)_4^-$	31,32
$[HPt(PR_3)_2(CH_3COCH_3)]^+PF_6^-$	$[anti\text{-}C_4H_7Pt(PR_3)_2]^+PF_6^-$	33,34
PR_3: $P(C_6H_5)_{3-n}(CH_3)_n$ ($n = 1,2$)		
$HPt(ClO_4)[P(C_6H_5)_3]_2$	$[anti\text{-}C_4H_7Pt[P(C_6H_5)_3]_2]^+ClO_4^-$	34
$[HMo(C_6H_5)_2L]_2 + NH_4PF_6$ ($L = \mu\text{-}C_6H_{11}MgBr_2Mg[O(C_2H_5)_2]$)	$[C_4H_7Mo(C_6H_5)_2]^+PF_6^-$	35,36
$[H_3Mo(C_6H_5)_2]^+PF_6^-$	$[C_4H_7Mo(C_6H_5)_2]^+PF_6^-$	37
$[HM(C_6H_5)_2Li]_4$ ($M = Mo, W$)	$[C_4H_7M(C_6H_5)_2]^+PF_6^-$	37,38

π-Crotyl(cyclo-octa-1,5-diene)rhodium is the product of the addition to butadiene of the intermediate hydride formed from (π-cyclohexenyl)(cyclo-octa-1,5-diene)-rhodium via the reaction [56]

$$(1.5\text{-}C_8H_{12})\,Rh\,(\pi\text{-}C_6H_9) \rightleftharpoons [(1.5\text{-}C_8H_{12})\,Rh\,(\pi\text{-}C_8H_8)]\,(H) \xrightarrow[+C_4H_6]{-C_6H_8} (1.5\text{-}C_8H_{12})\,Rh\,(C_4H_7)\,.$$

The intermediate nickel hydride complexes arising in the reduction of $NiCl_2$ by tri-isobutylaluminium react in succession with several butadiene molecules, giving rise to allyl complexes of nickel with the oligomeric π-allyl ligand [57]. The reactions involving the addition of hydride complexes of transition metals to butadiene with formation of intermediate π- or σ-crotyl complexes take place in the hydrogenation of butadiene under the influence of the pentacyanocobalt ion [58–69] and also in the codimerisation of butadiene with α-olefins in the presence of transition metal compounds capable of forming active metal–hydrogen bonds under the conditions of the synthesis [70–84].

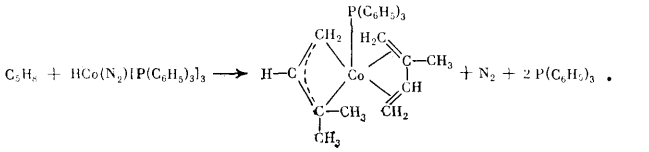
2. Isoprene and Chloroprene

Hydridopentacarbonylmanganese reacts with isoprene and chloroprene to form 1,4-σ-adducts close to room temperature [3]:

$$H_2C{=}\underset{\displaystyle X}{\underset{|}{C}}{-}CH{=}CH_2 + HMn(CO)_5 \rightarrow H_3C{-}\underset{\displaystyle X}{\underset{|}{C}}{=}CH{-}CH_2Mn(CO)_5,\ X = CH_3,\ Cl\ .$$

The iron hydride $HFe(CO)_4SiCl_3$ reacts similarly with isoprene [9].

According to ^1H NMR data, the only product of the interaction of isoprene with the ion $[HCo(CN)_5]^{3-}$ under the conditions of the hydrogenation reaction is the α-3-methylbut-2-enyl complex $[(CH_3)_2C{=}CHCH_2Co(CN)_5]^{3-}$. [88] This structure of the σ-allyl adducts of manganese, iron, and cobalt agrees satisfactorily with the 1,1-dimethyl-π-allyl structure of the complexes formed directly from the diene and the metal hydride under conditions promoting the elimination of one of the ligands. The interaction of isoprene with $HMn(CO)_5$ and $HFe(CO)_4SiCl_3$ at 95 °C yields immediately 1,1-dimethyl-π-allyl complexes [3,9]. The iron and cobalt hydrides $HFe(NO)(CO)_3$ [7,8] and $HCo(CO)_4$ [13] add similarly. It has been shown [85] that $HCo(N_2)[P(C_6H_5)_3]_3$ reacts with two isoprene molecules, one of which is inserted in the Co–H bond and the other is coordinated to cobalt, displacing a nitrogen molecule and two triphenylphosphine molecules:



This complex can also be obtained by the interaction of isoprene with cobalt hydride formed *in situ* (in the reduction of an ethanol solution of $CoCl_2$ by metallic zinc in the presence of triphenylphosphine) [42,86].

Table 2. The insertion of butadiene in transition metal–hydrogen bonds at the instant of their formation on reduction of metal compounds in the presence of butadiene.

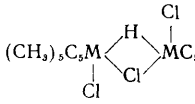
Initial compounds	Reaction product	References
$CoCl_2 + NaBH_4 + C_2H_5OH$	$C_8H_{13}CoC_4H_6$	39–41
$CoCl_2 + Zn + P(C_6H_5)_3 + C_2H_5OH$	*anti-* $C_4H_7Co(C_4H_6)P(C_6H_5)_3$	42,43
Cathodic reduction of $CoCl_2 + P(n\text{-}C_4H_9)_3$	$C_4H_7Co(C_4H_6)P(n\text{-}C_4H_9)_3$	44
$CoBr_2L_2 + NaBH_4 + NaX + CH_3OH$ *	$[(syn\text{-}C_4H_7)_2CoL_2]^+X^-$	45
$CoCl_2 \cdot 6H_2O + L_2 + NaBH_4 + NaX + CH_3OH$ *	$[(syn\text{-}C_4H_7)\ (anti\text{-}\ C_4H_7)CoL_2]^+X^-$	46
$NiCl_2 + Zn + P(C_6H_5)_3 + C_2H_5OH + C_6H_6$	$[syn\text{-}C_4H_7Ni[P(C_6H_5)_3]_2]^+ZnCl_3^-$	47
$[P(C_6H_5)_3]_4Ni + HCl$	$(syn\text{-}C_4H_7Ni[P(C_6H_5)_3]Cl$	48
$RhCl_3 + C_2H_5OH$	$(syn\text{-}C_4H_7RhCl_2)_2C_4H_6$	49–51
$[(C_2H_4)_2RhCl]_2 + HCl + C_2H_5OH$	$(syn\text{-}C_4H_7RhCl_2)_2C_4H_6$	52
$RhCl_3 \cdot 3H_2O + Zn + C_2H_5OH$	$[syn\text{-}C_4H_7RhCl_2(H_2O)]_2$	53
$[(CH_3)_5C_5MCl_2]_2 + Na_2CO_3 + C_2H_5OH$ ($M = Rh, Ir$)	$syn\text{-}C_4H_7MCl[C_5(CH_3)_5]$	54
$H_2IrCl_6 + C_2H_5OH$	$(syn\text{-}C_4H_7IrCl_2)_2C_4H_6$	55

*L_2 = 2,2′-bipyridyl or 1,10-phenanthroline; X = ClO_4 or PF_6.

According to Kruck et al. [87], the hydride $HCo(PF_3)_4$ adds to isoprene with formation of a 1,1-dimethyl-π-allyl adduct. Nixon and coworkers [88] observed that cobalt and rhodium complexes of this type readily undergo a skeletal isomerisation to 1,2-dimethyl-π-allyl complexes [26,89]. It is of interest that *anti*-1,2-dimethyl-π-allyltrifluorophosphine complexes of cobalt and rhodium are isomerisation intermediates. However, the *anti*-isomer of the rhodium complex is rapidly converted into the *syn*-isomer. On the other hand, the hydride $HRh(PF_3)_4$ adds to isoprene

with the immediate formation of the *anti*- and *syn*-1,2-dimethyl-π-allyl adducts[28]; the ratio of the *anti*- and *syn*-isomers depends on the temperature conditions in the reactions.

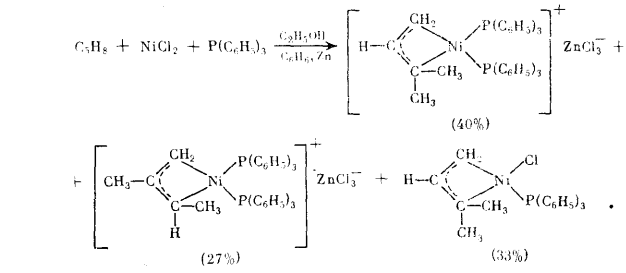
The iridium compound $HIr(CO)_2[P(C_6H_5)_3]_2$,[23] the titanium compound $[HTi(C_5H_5)_2]_2$,[20] the vanadium compound $HV(CO)_6$,[21,22] the palladium compounds $[HPdL_2]^+PF_6^-$ (L_2 = diphenylphosphinoethane or diphenylarsinoethane),[90,91] and the rhodium and iridium complexes



[29] react with isoprene like the rhodium complexes. On the other hand, the vanadium hydride complexes $HV(CO)_4L_2$ (L_2 = bisdiphenylarsinomethane or 1-diphenylarsino-2-diphenylphosphinoethane) add to isoprene with the preferential formation of 1,1-dimethyl-π-allyl complexes[92].

A mixture of adducts of the nickel hydride $\{HNi.[P(OCH_3)_3]_4\}^+HSO_4^-$ and isoprene contains mainly the *anti*-1,2-dimethyl-π-allyl complexes[18]. The fraction of 1,1-dimethyl-π-allyl adducts does not exceed 20%. Under these conditions, chloroprene forms exclusively $\{syn$-1-methyl-2-chloro-π-allyl-$Ni[P(OCH_3)_3]_3\}^+HSO_4^-$.

The mode of reaction of isoprene with nickel hydride complexes, formed in the reduction of nickel chloride by metallic zinc in the presence of bases, differs significantly from that observed by Tolman[18]. The amount of 1,1-dimethyl-π-allyl complexes is in this case much greater[47]:



On the other hand, when this reaction is carried out in acetonitrile, the only product is the 1,1-dimethyl-π-allyl adduct.

The codimerisation of isoprene with ethylene (in the presence of a catalyst comprising a nickel halide complex of trialkylphosphine + dialkylaluminium chloride) leads to the formation of *cis*-4-methylhexa-1,4-diene,[78] which indicates the occurrence of the reaction via an intermediate *anti*-1,2-dimethyl-π-allyl adduct of nickel hydride and isoprene. When a rhodium catalyst is used, the product is the *syn*-1,2-dimethyl-π-allyl complex, responsible for the formation of *trans*-4-methylhexa-1,4-diene from isoprene and ethylene[52]. The reactions involving the insertion of isoprene in the metal–hydride bond with formation of allyl complexes also occur when it [isoprene] is reduced by potassium iron carbonylate[93], in carbonylation under the influence of palladium catalysts[94], and in polymerisation in the presence of rhodium nitrate[95].

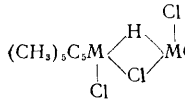
3. Penta-1,3-diene, Its Homologues, and Penta-1,4-diene

Penta-1,3-diene combines with transition metal hydrides, forming preferentially 1,3-dimethyl-π-allyl complexes regardless of the nature of the transition metal.

Among the adducts of hydridotetracarbonylcobalt and penta-1,3-diene, both *syn,anti*-, and *syn,syn*-1,3-dimethyl-π-allylcobalt tricarbonyls (with the latter predominating) were found[13,96-98]. The cobalt hydride, obtained by the reduction of $CoCl_2$ with zinc, reacts with penta-1,3-diene similarly[88].

The relative contents of the *syn,syn*- and *syn,anti*-structures depend primarily on the reaction temperature. The reaction of $HRh(PF_3)_4$ with penta-1,3-diene at 0°C leads to the formation of both isomers in nearly equimolar proportions. An increase of temperature promotes an increase of the yield of the *syn,syn*-1,3-dimethyl-π-allyl adducts. The influence of temperature has been demonstrated particularly clearly by Tolman[18], who showed that the addition of $\{HNi[P(OCH_3)_3]_4\}^+HSO_4^-$ to penta-1,3-diene at 0°C leads to $\{syn,anti$-1,3-dimethyl-π-allyl-Ni$.[P(OCH_3)_3]_3\}^+HSO_4^-$, whereas at 50°C 80% of the total amount of the 1,3-dimethyl-π-allyl complexes are in the *syn,syn*-configuration.

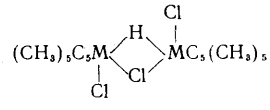
Only the *syn,syn*-1,3-dimethyl-π-allyl ligands were present in the complexes $C_5H_9Ti(C_5H_5)_2$[19,20,99-102] and $[C_5H_9PdL_2]^+PF_6^-$ (L_2 = diphenylphosphinoethane or diphenylarsinoethane)[90,91], synthesised by the reaction of penta-1,3-diene with the corresponding titanium and palladium hydrides. The *syn,syn*-1,3-dimethyl-π-allyl complexes of rhodium and iridium are the main products of the interaction of penta-1,3-diene with the complexes



;[29] but in these instances only 15% of the complexes with the 1-ethyl-π-allyl ligand are formed. Reactions involving the insertion of penta-1,3-diene in metal–hydride bonds also occur when it polymerises under the influence of rhodium chloride[103] and is hydrogenated in the presence of $RuCl_2[P(C_6H_5)_3]_3$.[104]

The influence of the position of the methyl substituents at the double bonds in penta-1,3-diene homologues on the rate and mode of reaction with the nickel hydride $\{HNi[P(OCH_3)_3]_4\}^+HSO_4^-$ was investigated by Tolman[18]. Table 3 shows that dienes with inner double bonds (hexa-2,4-diene and 2,5-dimethylhexa-2,4-diene) exhibit the lowest reactivity. 2-Methylpenta-1,3-diene is five times less reactive than penta-1,3-diene; the presence of substituents at the inner double bond makes the difference between the rates less significant.

The titanium hydride $[HTi(C_5H_5)_2]_2$ reacts with 3-methylpenta-1,3-diene similarly to nickel hydride[20]. On the other hand, the mode of reaction of the iridium hydride $HIr(CO)_2[P(C_6H_5)_3]_2$ with 2,4-dimethylpenta-1,3-diene differs from that indicated in Table 3 for nickel hydride—the product is 1-isopropyl-2-methyl-π-allyldicarbonyltriphenylphosphineiridium[23]. Rhodium and iridium complexes of the type



react with 2-methylpenta-1,3-diene and 2,5-dimethylhexa-2,4-diene to form compounds with 1,1,3-trimethyl- and 3-isopropyl-1,1-dimethyl-π-allyl ligands[29]. However, when the former diene reacts with the rhodium complex, approximately 20% of *syn*-1-ethyl-2-methyl-π-allyl-RhCl$.[C_5(CH_3)_5]$ is also formed.

Only $HCo(CO)_4$ adds to penta-1,4-diene; in this instance a mixture of *syn*- and *anti*-1-ethyl-π-allylcobalt tricarbonyls with an admixture of the 1,3-dimethyl-π-allyl complexes was isolated[96-98]. Under the influence of the

rhodium hydride $HRh(PF_3)_4$,[28] the titanium hydride $[HTi(C_5H_5)_2]_2$,[20], and the nickel hydride $HNi[P(OCH_3)_3]_4 \cdot HSO_4$,[18] penta-1,4-diene initially isomerises to penta-1,3-diene. Subsequently the reaction proceeds via the pathway indicated above.

Table 3. Reactions of $HNi[P(OCH_3)_3]_4HSO_4$ with dienes[18].

Diene	Structure of π-allyl ligand in reaction products	$\tau^*_{1/2}$, h (t, °C)
Penta-1,3-diene (mixture of *cis*- and *trans*-forms)	*syn, anti*-1,3-dimethyl-π-allyl *syn, syn*-1,3-dimethyl-π-allyl	0.3 (0)
trans-3-Methylpenta-1,3-diene	*syn, anti*-1,2,3-trimethyl-π-allyl *syn, syn*-1,2,3-trimethyl-π-allyl	0.5 (0)
trans-2-Methylpenta-1,3-diene	*syn*-1,1,3-trimethyl-π-allyl	1.5 (0) 0.2 (25)
2,4-Dimethylpenta-1,3-diene	1,1,3,3-tetramethyl-π-allyl	0.4 (25)
Hexa-2,4-diene (mixture of *trans, trans*-, *cis, trans*-, and *cis, cis*-forms)	*anti*-1-ethyl-*syn*-3-methyl-π-allyl *syn*-1-ethyl-*syn*-3-methyl-π-allyl	0.5 (25) 0.5 (25)
2,5-Dimethylhexa-2,4-diene	3-isopropyl-1,1-dimethyl-π-allyl	1.5 (25)

*50% reaction time.

The higher rate of reaction of hydrides with conjugated dienes compared with non-conjugated dienes readily explains the finding that in the codimerisation of 1,3-dienes with α-olefins the hydrides react with 1,3-dienes to form π-allyl complexes.

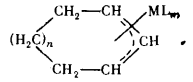
4. 2,3-Dimethylbutadiene

The addition of transition metal hydrides to 2,3-dimethylbutadiene leads to complexes with a 1,1,2-trimethyl-π-allyl ligand. These reactions have been described only for cobalt-group (cobalt[13] as well as rhodium and iridium[29]) hydrides. The iron hydride $HFe(CO)_4SiCl_3$ reacts with 2,3-dimethylbutadiene to form only the σ-adduct[9].

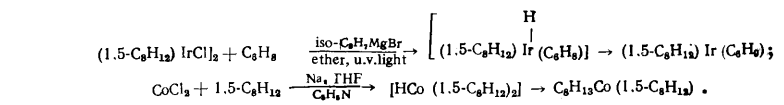
The nickel complexes $\{C_6H_{11}Ni[P(C_6H_5)_3]_2\}^+ZnCl_3^-$ and $C_6H_{11}Ni[P(C_6H_5)_3]Cl$ have been obtained as a result of the addition to 2,3-dimethylbutadiene of the nickel hydride formed in the reduction of $NiCl_2$ by zinc in the presence of triphenylphosphine[47].

5. Cyclic Diene Hydrocarbons

Table 4 presents the structures of the adducts of transition metal hydrides and cyclic dienes, which are complexes with π-allyl cyclic ligands having the general form



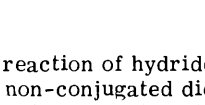
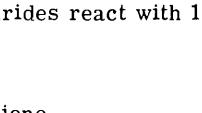
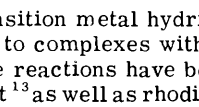
π-Cyclohexenyl-π-cyclo-octa-1,5-dieneiridium[108] and π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt[86] were obtained as a result of the addition of the intermediate metal hydrides to cyclohexa-1,3-diene and cyclo-octa-1,5-diene respectively:



6. Allene Hydrocarbons

Allene is very readily inserted in a metal–hydrogen bond. The addition of hydrogen leads solely to an *sp*-hybridised carbon atom and π-allyl complexes are formed. The pentacoordinate trigonal-bipyramidal rhodium and iridium complexes $HRh(CO)[P(C_6H_5)_3]_3$ and $HIr(CO)_2[P(C_6H_5)_3]_2$ react with allene to form the complexes $C_3H_5M(CO)[P(C_6H_5)_3]_2$ having the same coordination number[23]. As in the reaction with butadiene, one of the equatorial ligands (triphenylphosphine in the former complex and carbon monoxide in the latter) is displaced. $HRh(PF_3)_4$ and allene give rise to the adduct $C_3H_5Rh(PF_3)_3$;[25,26] $HV(CO)_6$ adds to allene to form π-allylpentacarbonylvanadium[22].

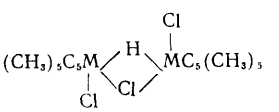
Table 4. Addition of cyclic dienes to transition metal hydrides.

Cyclic diene	Initial hydride complex	Reaction product	Refs.
Cyclopentadiene	$HNi[P(OCH_3)_3]_4HSO_4$	$C_5H_7Ni[P(OCH_3)_3]_3HSO_4$	18
Cyclopentadiene	$HPdL_2PF_6$*	$C_5H_7PdL_2PF_6$*	90,91
Cyclopentadiene	 (M=Rh, Ir)	$C_5H_7M[C_5(CH_3)_5]Cl$	105
Cyclohexa-1,3-diene	$HCo(CO)_4$	$C_6H_9Co(CO)_3$	106
Cyclohexa-1,3-diene	$HRh[P(C_6H_5)_3]_4$	$C_6H_9Rh[P(C_6H_5)_3]_2$	24
Cyclohexa-1,3-diene	$HRh(PF_3)_4$	$C_6H_9Rh(PF_3)_3$	25,26
Cyclohexa-1,3-diene	 (M=Rh, Ir)	$C_6H_9M[C_5(CH_3)_5]Cl$	105
Cyclohexa-1,3-diene	$HPdL_2PF_6$*	$C_6H_9PdL_2PF_6$*	90,91
Cyclohexa-1,3-diene	$H_2Mn_2(CO)_{12}$	$C_7H_{11}Mn(CO)_4$	107
Cyclo-octa-1,3(1,5)-diene	 (M=Rh, Ir)	$C_8H_{13}M[C_5(CH_3)_5]Cl$	27,105
Cyclo-octa-1,3(1,5)-diene	$HPdL_2PF_6$*	$C_8H_{13}PdL_2PF_6$*	90,91
Cyclo-octa-1,3(1,5)-diene	$HPh[P(C_6H_5)_3]_4$	$C_8H_{13}Rh[P(C_6H_5)_3]_2$	24

*L_2 = diphenylphosphinoethane or diphenylarsinoethane.

When allene was allowed to react with a solution of *trans*-$HPt(NO_3)[P(C_2H_5)_3]_2$ and $NaB(C_6H_5)_4$ in methanol, the complex $\{C_3H_5Pt[P(C_2H_5)_3]_2\}^+B(C_6H_5)_4^-$ was isolated[31,32]. The reaction of allene with *trans*-$HPt(CH_3OH)[P(C_6H_{11})_3]_2 \cdot PF_6$ led to an analogous π-allyl complex[109].

The hydride complexes of rhodium and iridium



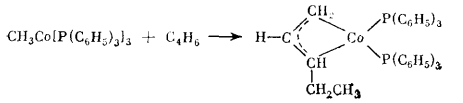
add to 1,1-dimethylallene, forming 1,1-dimethyl-π-allyl complexes[29]. The insertion of the coordinated methylallene in the metal–hydride bond in the intermediate complex, arising in the interaction of π-indenyl-π-dimethylacetylenebis(trimethyl phosphite)molybdenum tetrafluoroborate with $NaBH_4$, leads to an anti-π-crotyl complex of molybdenum[110].

III. INSERTION IN TRANSITION METAL–CARBON σ-BONDS

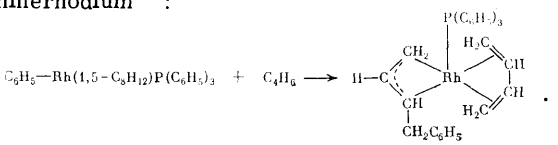
As a rule, alkyl compounds of transition metals are characterised by a low stability which naturally restricts the range of their reactions with unsaturated hydrocarbons.

1. Conjugated Dienes

Only one example of a stoichiometric reaction involving the insertion of butadiene in a transition metal–alkyl bond is known at the present time [111]:

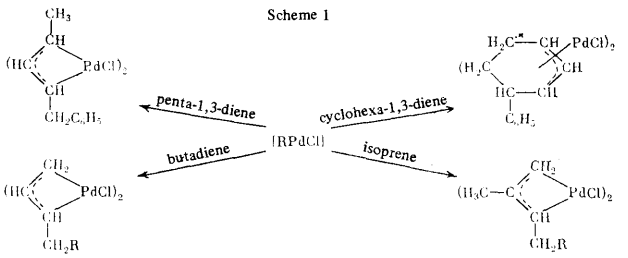


The geometrical configuration of the 1-ethyl-π-allyl ligand in this complex was not established by the authors. Butadiene also adds to phenyl(cycloocta-1,5-diene)triphenylphosphinerhodium [112]:



Alkyl- and allyl-palladium chlorides, obtained from $LiPdCl_3$ and the corresponding mercury, magnesium, or tin compounds, react with conjugated dienes to form π-allyl adducts [113]:

Scheme 1



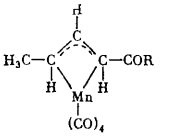
R = CH_3, C_6H_5, *p*-anisyl, or 1-naphthyl

R = C_6H_5 or $C_6H_5CH_2$

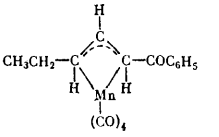
The structure of the adducts in Scheme 1 leads to the conclusion that the mode of insertion of isoprene in Pd–C σ-bonds is the same as in its addition to Pd–H and Pd–acido-ligand bonds (see below).

σ-Alkyl and aryl derivatives of manganese, cobalt, and iron carbonyls readily react with 1,3-diene hydrocarbons. The addition reaction is preceded by the conversion of the organometallic compound into an acyl form: the diolefin molecule is inserted in the metal–acyl [M–C(O)–] bond (Tables 5 and 6). The data in Tables 5 and 6 show that the mode of addition of acylmetal carbonyls is determined by the nature of the transition metal in the initial methyl- or acyl-metal carbonyls. Whereas the *cis*-double bond is the most reactive in cobalt complexes and the acyl ligand is attached to the terminal carbon atoms in transoid diolefins, iron complexes react with *cis*-penta-1,3-diene and isoprene to form 1,3- and 1,1-disubstituted π-allyl adducts respectively.

Phenyl- and methyl-manganese pentacarbonyls react with butadiene and *trans*-penta-1,3-diene to form the π-allyl complexes (I) and (II) respectively [118–121]:



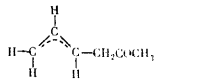
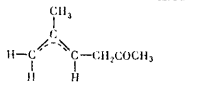
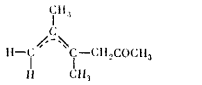
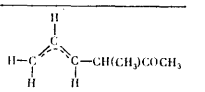
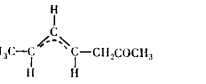
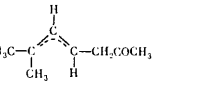
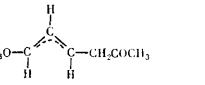
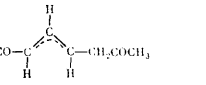
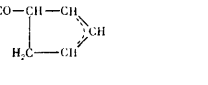
(I)



(II)

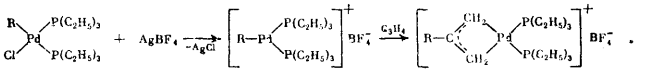
R = CH_3 or C_6H_5 .

Table 5. π-Allylcobalt tricarbonyl formed from dienes and $CH_3Co(CO)_4$ or $CH_3COCo(CO)_4$. [114–117]

Diene	Structure of π-allyl ligand
Butadiene	
Isoprene	
2,3-Dimethylbutadiene	
cis-Penta-1,3-diene	
trans-Penta-1,3-diene	
4-Methylpenta-1,3-diene	
trans-1-Methoxybutadiene	
Methyl sorbate	
Cyclopentadiene	

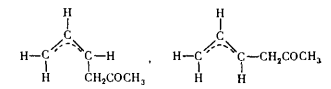
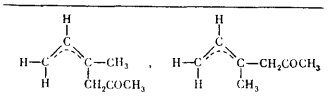
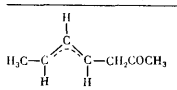
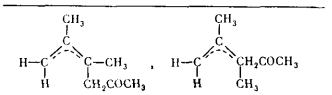
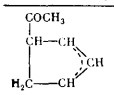
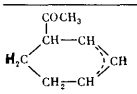
2. Cumulated Dienes

Allene is inserted in the Pt–CH_3 bond with formation of 2-methyl-π-allyl complexes [122–124]. The coordination-unsaturated methyl- or phenyl-bis(triphenylphosphine)-palladium tetrafluoroborates add very readily to allene [125]:

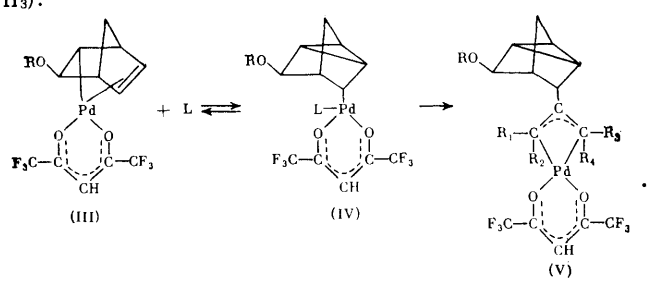


The reactions of cationic vinylplatinum complexes $\{Pt(R^1{=}C{=}CHR^2)[P(OC_2H_5)_3]_2(CH_3COCH_3)\}^+PF_6^-$ (R^1 = CH_3, CF_3, or $COOCH_3$; R^2 = CH_3, CF_3, C_6H_5, $COOCH_3$ or cyclo-C_6H_{11}) react with allene also to form π-allyl products with a 2-alkenyl substituent in the π-allyl ligand [126]. Acyltricarbonylcobalt reacts with allene to form π-allyl complexes containing an acyl group at the central carbon atom of the allyl group [127].

Table 6. The structure of the π-allyl ligands in the iron complexes formed in reactions of $NaFe(NO)(CO)_3$ and CH_3I in the presence of dienes [8].

Diene	Structure of π-allyl ligand
Butadiene	
Isoprene	
cis-Penta-1,3-diene	
2,3-Dimethylbutadiene	
Cyclopentadiene	
Cyclohexa-1,3-diene	

Allene and 1-methyl-, 1,1-dimethyl-, and 1,3-dimethylallenes are inserted in the palladium–nortricyclenyl ligand σ-bond in complexes (IV) (L = 1,2-diene) arising when allenes react with complexes (III) (R = CH_3CH_2CO or C_6H_5CO). This results in the formation of the corresponding π-allyl complexes (V) (R_1, R_2, R_3, R_4 = H or CH_3): [128]



(III) (IV) (V)

Conjugated dienes (butadiene, isoprene, 2,3-dimethylbutadiene, and *cis*- and *trans*-pentadienes) also readily form complexes of type (IV), in which L is a 1,3-diene coordinated as a monodentate species. However, in contrast to allene, they are not inserted in a Pd–C bond.

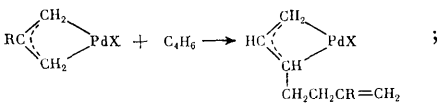
IV. ADDITION OF DIENES TO π-ALLYL METAL–CARBON BONDS

The discovery in 1964 of the catalytic activity of the π-allyl complexes of nickel in the polymerisation of 1,3-diolefins [129,130] initiated the systematic investigation of these reactions. However, in the present review we shall not consider in detail the extensive data accumulated at the present time on the polymerisation of dienes under the influence of π-allyl transition metal complexes, attention being concentrated on studies in which the structures of the products of the addition of the 1,3-dienes to the metal–π-allyl ligand bond were rigorously established.

1. Butadiene

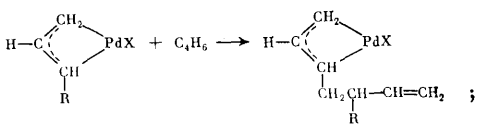
Bis-(π-crotylnickel halides) add stereo- and regioselectively to butadiene [131]. Regardless of the nature of the halogen atom, the addition takes place with participation of only the bond between nickel and the unsubstituted carbon atom of the allyl group. Frequent repetition of such steps leads to the formation of polybuta-1,4-diene. The individual stages of this process were investigated in relation to the reactions of bis-(π-crotylnickel iodide) and its deuterated analogues with butadiene, 1,1,4,4-tetradeuterobutadiene, and perdeuterobutadiene [132–141].

The π-allyl complexes of palladium react with butadiene to form 1 : 1 adducts [142–150]:



R = H, CH_3, Cl, $COOCH_3$, or t-C_4H_9; X = acido-ligand.

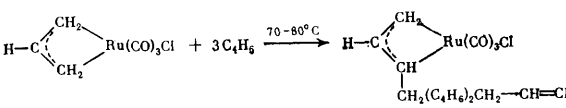
Regardless of the nature of the substituent (R = CH_3, CH_2Cl, Cl, $COOCH_3$, or C_6H_5), in reactions with 1-substituted π-allylpalladium complexes butadiene attacks only the substituted carbon atom of the allyl ligand [143–146,149]:



X = Cl, Br, or hexafluoroacetylacetonate.

When the last two reactions are carried out at a high temperature and a high concentration of the reactants, there is a possibility of the polymerisation of the 1,3-diene [144–146,151–153].

π-Allyltricarbonylruthenium chloride reacts with butadiene to form the product of the insertion of three diene molecules at once [154]:

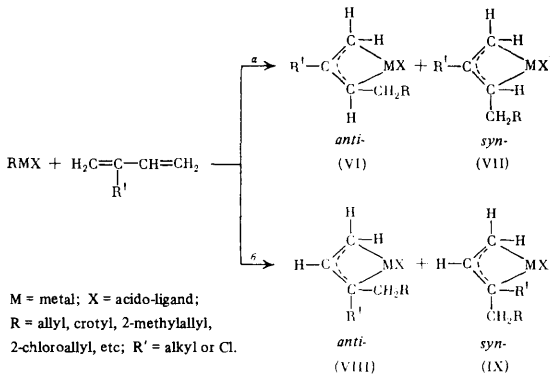


According to infrared spectroscopic data [154], the butadiene units of the complex have the *trans*-1,4-structure.

2. 2-Alkyl-Substituted 1,3-Dienes and Chloroprene

The reactions of these asymmetric dienes with π-allyl complexes of transition metals can lead theoretically to the formation of π-allyl adducts of four types:

Scheme 2

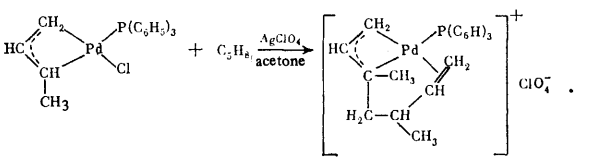


Bis-(π-crotylnickel iodide) reacts with isoprene via both pathways (*a* and *b*). The total fraction of *anti*- and *syn*-1,2-disubstituted complexes (VI) and (VII) is approximately 90%.[155-157] The ratio of these isomers changes during the reaction and tends to a limit, which depends on temperature. During the first period, only the *anti*-complexes (VI) are detected in solution[158,159], but subsequently the latter isomerise to the *syn*-adducts.

The reactions with 2-ethyl-, 2-isopropyl-, and 2-t-butyl-butadienes proceed wholly via pathway *a*.[158-160] The nature of the alkyl substituent has a very significant influence on the ratio of the *anti*- and *syn*-isomers formed. For a long time after the start of the interaction of $(C_4D_7NiI)_2$ with 2-ethyl- and 2-isopropyl-butadienes the concentration of the *anti*-isomers greatly exceeds that of the *syn*-isomers. On the other hand, the adduct of $(C_4D_7NiI)_2$ with 2-t-butylbutadiene exists in the *anti*-configuration (VI) (R′ = t-C_4H_9; R = C_4D_7). The ^{13}C NMR spectra of the 1 : 1 *anti*- and *syn*-adducts of crotylnickel iodide and 2-alkylbutadienes provide an idea about the nature of the distribution of electron density over the π-allyl carbon atoms[161].

In contrast to π-crotylnickel iodide, the π-allyl complexes of palladium react with isoprene only via pathway *b*, yielding 1,1-disubstituted π-allyl complexes (VIII) and (IX) (R′ = CH_3).[143-146,149,162-164] The fraction of the *anti*-isomers (VIII) in the adducts of π-allyl- and π-methylallylpalladium bromides and isoprene is approximately 80%,[146] while bis-(2-chloro-π-allylpalladium chloride)[146,162,163] and 2-chloro-π-allylpalladium hexafluoroacetylacetonate[148] give rise to approximately equal proportions of the *anti*- and *syn*-isomers (VIII) and (IX) (R′ = CH_3, R = CH_2–$CCl=CH_2$). 2-Chloro-π-allylpalladium chloride adds to 2-t-butylbutadiene with formation of a 1,1-disubstituted π-allyl complex in which the chlorobutenyl group is only in the *anti*-position[165].

Structure (X) with a coordinated vinyl group has been proposed for the product of the reaction of π-crotyltriphenylphosphinepalladium chloride with isoprene in the presence of $AgClO_4$, but accurate data for the structure of this compound are not quoted[166]:

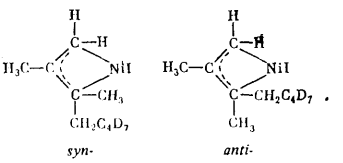


(X)

Chloroprene reacts with π-allyl complexes of palladium like isoprene, forming a mixture of the *syn*- and *anti*-isomers of 1,1-disubstituted π-allyl complexes[146,163].

3. 2,3-Dimethylbutadiene

On interaction with 2,3-dimethylbutadiene, π-allyl complexes of nickel and palladium form adducts containing 1,1,2-trisubstituted π-allyl ligands. The ^1H NMR spectrum of the adduct of $(C_4D_7NiI)_2$ and 2,3-dimethylbutadiene showed the presence in solution of complexes having the *syn*- and *anti*-structures[141,160]:

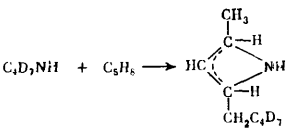


syn- *anti*-

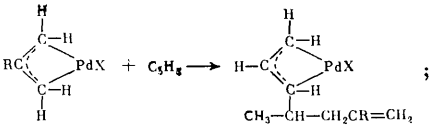
The adducts of the π-allyl complexes of palladium also consisted of a mixture of the *syn*- and *anti*-isomers[149]. In 1-substituted π-allyl complexes of palladium a new carbon–carbon bond is formed between the methylene group of the diene and the substituted carbon atom of the allyl group.

4. Penta-1,3-diene and 4-Methylpenta-1,3-diene

The *cis*- and *trans*-penta-1,3-diene isomers react differently with π-allyl complexes of nickel and palladium. The allyl ligand in the nickel complexes adds to the terminal methylene group of the diene[141,160]:

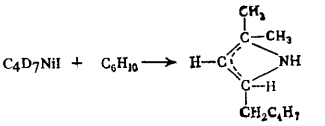


Palladium compounds react with pentadiene, forming 1-substituted π-allyl adducts[146-149]:



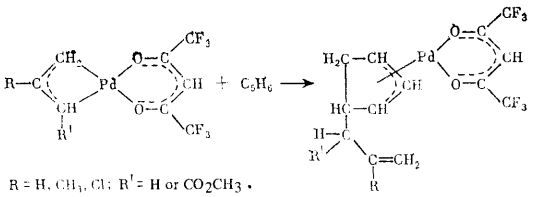
R = H, Cl; X = Cl or hexafluoroacetylacetonate.

[D_7]π-Crotylnickel iodide reacts with 4-methylpenta-1,3-diene to form the 1,3,3-trisubstituted *syn*-π-allyl complex[141,160]:



5. Cyclic 1,3-Dienes

On interaction with π-allyl complexes of palladium, cyclopentadiene forms π-cyclopentenyl compounds[149]:

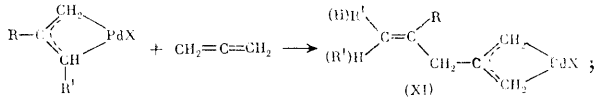


R = H, CH_3, Cl; R' = H or CO_2CH_3.

Palladium 2-chloro-π-allylhexafluoroacetylacetonate adds to cyclohexa-1,3-diene to form the corresponding π-cyclohexenyl complex. Cyclo-octa-1,3-diene is not inserted in the palladium–allyl ligand bond[146,149].

6. Allenes

In contrast to conjugated dienes, allene react with π-allyl complexes of palladium, adding to the less substituted terminal carbon atom of the allyl group[146,148]:

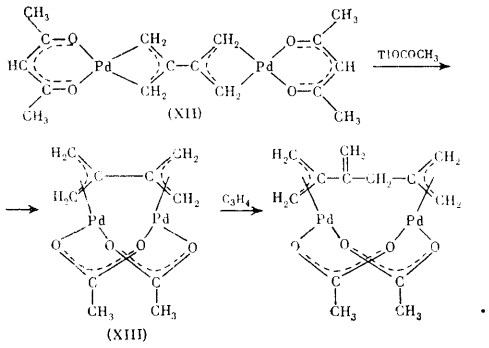


(XI)

R = H, CH_3, or Cl; R' = H, CH_3, Cl, or $COOCH_3$; X = acetylacetonate or Cl.

It is of interest to note that the product of the reaction of bis-(1-chloro-π-allylpalladium chloride) with allene is a mixture of *cis*- (80%) and *trans*-isomers (20%) of compound (XI) (R = H, R' = Cl),[146] which shows that the 1-chloro-π-allyl ligand in the initial complex exists predominantly in the *anti*-configuration.

Interaction of π-allylpalladium acetylacetonate with allene results in the formation of compound (XII) in addition to complex (XI) (R = R' = H).[167] If the acetylacetonate ligand in the former compound is replaced by the acetate ligand, the three-bridge complex (XIII) formed under these conditions can combine with yet another allene molecule[168,169]:



(XIII)

The reactions involving the insertion of allene in the bond between the nickel atom and the π-allyl ligand take place in the cyclic oligomerisation of allene by nickel[170–174] and rhodium[175] complexes.

Summarising the available experimental data, it is possible to set up activity series for reactions involving the addition of π-allyl complexes of nickel[141,155–160] and palladium[143,146,149] to 1,3-dienes (Table 7). The data in Table 7 show that the mode of addition of π-allyl complexes of nickel and palladium to diolefins is determined by the nature of the transition metal and the acido-ligand links to it. All the addition reactions examined are characterised by high regio- and stereo-selectivity. Isoprene reacts with nickel derivatives faster than does butadiene; in relation to the palladium analogues, butadiene is more reactive. Among π-allylpalladium halides, the chlorides are more reactive than the iodides; allylnickel iodides react more readily with dienes than do the chlorides.

Table 7. The activity series in the formation of 1 : 1 adducts of the π-allyl complexes of nickel and palladium and 1,3-dienes.

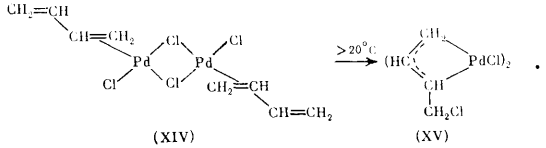
Pd complexes	Ni complexes
Dienes	
Butadiene > isoprene > chloroprene > *trans*-penta-1,3-diene > 2,3-dimethylbutadiene > cyclopentadiene > cyclohexadiene > *cis*-penta-1,3-diene > 2,5-dimethylhexa-2,4-diene	Butadiene < isoprene < 2-ethylbutadiene < 2-isopropylbutadiene < 2-t-butylbutadiene
Substituents in π-allyl ligand	
2-Chloro- > 2-methoxycarbonyl > 1-chloro- > 1-methoxycarbonyl > H > 2-methyl > 1-methyl > 1-phenyl > 2-t-butyl	H > 2-methyl > 2-ethyl > 2-isopropyl ≫ 2-t-butyl
Acido-ligands	
Hexafluoroacetylacetonate > acetylacetonate > Cl > Br > SCN > I	Cl < Br < I

In the palladium complexes a diene molecule attacks the most substituted of the terminal carbon atoms of the π-allyl ligand, while in the reaction of π-crotylnickel halides a new carbon–carbon bond is formed with participation of the unsubstituted carbon atom. Asymmetric 1,3-dienes (isoprene and pentadiene) form adducts with different structures of the π-allyl ligand; palladium forms 1,1-disubstituted and nickel mainly 1,2-disubstituted π-allyl complexes.

V. INSERTION OF DIENES IN TRANSITION METAL–ACIDO-LIGAND BONDS

1. Conjugated Dienes

Addition reactions of this type have been described only for palladium compounds. The interaction of butadiene with the palladium salts $(C_6H_5CN)_2PdCl_2$, $PdCl_2$, and $[(olefin)PdCl_2]_2$ at temperatures below −40°C leads to the quantitative formation of the dimeric complex (XIV):[176]



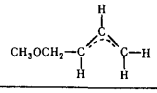
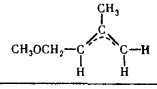
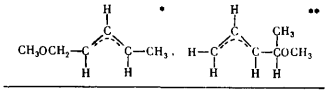
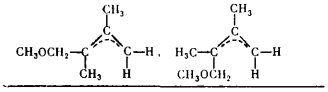
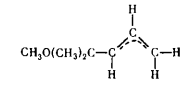
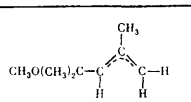
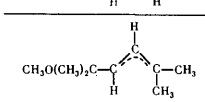
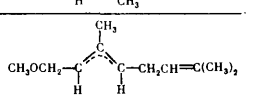
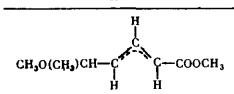
(XIV) (XV)

When the complex (XIV) is heated above 20°C or the interaction of butadiene with the palladium salt is carried out above room temperature, the formation of the π-allyl complex (XV), which is a product of the insertion of the

coordinated butadiene in the Pd–Cl bond, is promoted[176,177]. The addition of palladium chloride to chloroprene takes place with formation of the dimeric 1-chloromethyl-2-chloro-π-allylpalladium chloride[178].

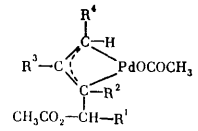
The mechanism of these reactions was studied by Lukas and coworkers[179,180] in relation to the formation of dimeric 1-(1-chloroethyl)-3-methyl-π-allylpalladium chlorides derived from the three isomers of hexa-2,4-diene. If the reaction of the palladium salts with dienes is carried out in an alcoholic medium, then its products are π-allyl complexes with alkoxy-groups. The structures of the π-allyl ligands in the complexes obtained as a result of the interaction of methanol solutions of palladium salts with various dienes are presented in Table 8. Certain cyclic dienes (for example, cyclohexa-1,3-diene) react similarly with palladium salts, giving rise to complexes with cyclic π-allyl ligands containing a methoxy-group in the ring[187]. The stability of these complexes is much lower than that of the corresponding acyclic analogues, which is due to the ease of elimination of the alcohol molecule.

Table 8. The structures of the π-allyl ligands in the complexes formed on interaction of 1,3-dienes with palladium salts in CH_3OH.

Diene	Structure of π-allyl ligand	Refs.
Butadiene		177,181, 182
Isoprene		181–184
Penta-1,3-diene		184
2,3-Dimethyl-butadiene		181
4-Methylpenta-1,3-diene		181
2,4-Dimethylpenta-1,3-diene		181
2,5-Dimethylhexa-2,4-diene		181
cis- or *trans*-Ocimene		185
Methyl sorbate		186

* Principal product at a reaction temperature of 50–60°C.
** Principal product at a reaction temperature of 0–10°C.

If the interaction of palladium salts with dienes is carried out in acetic acid, complexes with the CH_2OCOCH_3 group at the terminal carbon atom of the allyl group are produced. Butadiene[184,188], isoprene[184,188], and 2,3-dimethylbutadiene[188] react in this way with palladium halides. The π-allyl complexes (XVI) are products of the interaction of palladium acetate with hexa-2,4-dienes ($R^1 = R^4 = CH_3$; $R^2 = R^3 = H$), 2,3-dimethylbutadiene ($R^1 = R^4 = H$; $R^2 = R^3 = CH_3$), and 2-t-butyl-5,5-dimethylhexa-1,3-diene ($R^1 = R^3 = t\text{-}C_4H_9$; $R^2 = R^4 = H$):[189]



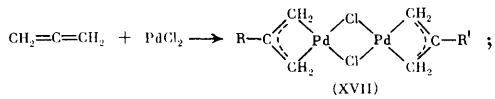
(XVI)

The reactions of diene hydrocarbons with palladium salts in alcoholic media or in acetic acid can be regarded formally as reactions involving the insertion of the diene in the palladium–acido-ligand bond. However, there is good reason to believe at the present time that the nucleophilic methoxide or acetate ions attack directly the diene ligand, resulting in the formation of complexes containing an ether or ester group respectively in the π-allyl ligand[179,183].

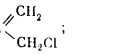
The π-allyl complexes with an alkoxy-substituent, generated from butadiene, isoprene, and pentadiene, are intermediates in the carbonylation of these dienes in the presence of palladium chloride[190,191]. The formation of 1-acetoxybutadiene and 1,4-diacetoxybut-2-ene from butadiene and palladium acetate in acetic acid proceeds via the intermediate 1-acetoxy-π-allyl palladium complex[192].

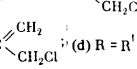
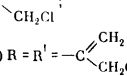
2. Cumulated Dienes

Allene and its homologues (methyl-, dimethyl-, and tetramethyl-allenes) react very readily with palladium chloride, giving rise to π-allyl complexes with various groups at the central carbon atom of the allyl group[182,193–197].



(XVII)

(a) R = R' = Cl; (b) R = R' =  ;

(c) R = Cl, R' =  ; (d) R = R' =  .

The structure of the resulting complex (XVIII) depends on the reaction conditions. If the allene is introduced into a benzene solution of $(C_6H_5CN)_2PdCl_2$, then the product is mainly bis-(2-chloro-π-allylpalladium chloride) (XVIIa). When benzonitrile or methylene chloride is used as the solvent, the complex (XVIIb) is formed; the same compound is produced when allene is passed through a methanol suspension of Na_2PdCl_4. The analogous reaction with $(C_6H_5CN)_2PdCl_2$ leads to approximately equal amounts of complexes (XVIIb) and (XVIId). A dimeric complex with two different π-allyl ligands (XVIIc) is obtained when $(C_6H_5CN)_2PdCl_2$ is introduced into a benzene solution of allene.

The interaction of allene with an acetic acid solution of Na_2PdCl_4 in the presence of sodium acetate leads to bis-(2-acetoxy-π-allylpalladium chloride) (XVII) (R = R′ = CH_3COO).[198] The same complex is a product of the reaction of palladium acetate with allene in benzene in the presence of aqueous NaCl.[199]

The mechanism of reactions of allene with palladium salts, discussed in a number of studies[193,195,197,200], is not altogether clear. Whereas the formation of the complex (XVIIa) apparently involves the simple insertion of allene in the Pd–Cl bond, products containing the dimerised allene can arise via different pathways. At any rate the formation of such complexes does not involve the insertion of a second allene molecule in the Pd–π-allyl bond of complex (XVIIa), because it has been established[197] that this reaction does not occur. Furthermore, such insertion would have resulted in a complex with a different structure of the π-allyl ligand. It has been suggested[197] that the second allene molecule is inserted in the Pd–C bond in the intermediate σ-complex $CH_2=C(CH_2Cl)-Pd-Cl$. There is also a possibility of the dimerisation of two allene molecules in the coordination sphere of palladium with subsequent migration of chlorine from palladium to carbon and the formation of compound (XVIIb).

VI. THE MECHANISM OF STEREOREGULATION IN REACTIONS INVOLVING THE INSERTION OF DIENES IN TRANSITION METAL–LIGAND BONDS

The reactions involving the insertion of dienes in transition metal–ligand bonds are characterised by high regio- and stereo-selectivities. This is due primarily to the fact, despite the significant differences in details, the above processes are based on a coordination mechanism. Preliminary coordination of the diolefin to the transition metal is a necessary condition for the subsequent addition. As a result of coordination, the molecule of the unsaturated compound is not only fixed in a particular configuration, which is responsible for the mode of the subsequent interaction, but, by virtue of its unusual energy state in such a complex, it acquires the ability to be inserted in the metal–ligand bond.

Before being inserted in the metal–ligand bond, the diene forms as a rule a π-complex only in the transition state, which hinders the direct experimental detection of such complexes. However, in a few instances it is possible to isolate intermediates (XIV) of this kind[176].

Preliminary coordination of the diene to the transition metal can be observed indirectly by NMR. For example, the coordination of the diolefin to the palladium atom in π-allylpalladium complexes is responsible for the very rapid merging of the signals due to the *syn*- and *anti*-protons at the terminal carbon atom of the allyl group[148,149,201–203]. The exchange of the *syn*- and *anti*-protons is apparently due to the monodentate coordination of the diene. This is indicated by the satisfactory agreement between the reactivities of many dienes in promoting the *syn*–*anti*-proton exchange[148] and in their reactions with 6-acetoxynorbornenylpalladium(III) hexafluoroacetylacetonate[128]: butadiene $\simeq$ ***cis***-penta-1,3-diene $\simeq$ ***trans***-penta-1,3-diene > isoprene > 2,3-dimethylbutadiene; under these conditions, asymmetric dienes are coordinated via the less substituted double bond.

The modern treatment of the nature of the bond in the π-complexes formed by the interaction of the metal with unsaturated compounds, devised by Dewar[204] and Chatt and Duncanson[205] in terms of the molecular orbital theory, has been discussed in many detailed reviews and monographs[206–213]. Here one need only emphasise that dative binding plays a special role in reactions of transition metals. According to the familiar classification of Langford and Gray[214] of ligand substitution reactions involving transition metal complexes, substances capable of dative interaction as a rule react via a bimolecular (associative) mechanism. The interaction between the antibonding orbital of the olefin (diene) and *d* electrons takes place over distances longer than the donor–acceptor bond. This should promote a decrease of the overall activation energy for the formation of the metal–substrate π-complex[212].

It follows from the foregoing that the capacity of the ligand for dative binding can give it an appreciable advantage in coordination to the metal even in comparison with substances having a greater electron-donating capacity and in the case of diolefins can be responsible also for the preferential coordination of the double bond with the lower electron density.

The role of the dative interaction in the formation of the π-complex of a diene and a transition metal can be demonstrated most strikingly in relation to the addition of dienes to bis-(π-allylnickel halides)[131]. The study of the reactions of butadiene with $(C_4H_7NiI)_2$ in a medium containing Lewis bases showed that they can be clearly divided into two groups in terms of their effect on the addition reaction. The first group comprises σ-donors (water, ethers, and tertiary amines), which do not influence the rate and mode of reaction regardless of their σ-donor capacity. The second group includes substances (trialkyl- and triaryl-phosphines or the corresponding phosphites and pyridine), which exhibit a π-acceptor capacity in addition to the σ-donor capacity. Depending on their π-acceptor capacity, the latter substances decrease the yield of adducts or, in the limiting case, fully suppress the addition reaction.

On the basis of these facts, the unique ability of bis-(π-crotylnickel iodide) to initiate the polymerisation of diolefins in an aqueous emulsion[215] can be explained not only by the hydrolytic stability of the nickel–carbon bond, but also by the fact that in the transition state of the reaction the dative binding of the transition metal to tne substrate plays a significant role. In view of the d^8 character of the nickel atom in bis-(π-crotylnickel iodide), the considerable strength of the Ni–I bond, the large *trans*-effect of the iodide anion, and the presence of a diolefin molecule in the coordination sphere of the metal, presumably the insertion process proceeds via an associative mechanism with a pentacoordinate transition state formed with participation of the p_z orbital of nickel[131].

The next stage in the process involving the insertion of the diene in the metal–ligand bond is intramolecular transformation of the π-complex, in the course of which the active ligand (hydrogen, alkyl, allyl, or an acido-group) is bound to one of the carbon atoms of the diene system and a new metal–carbon bond is formed.

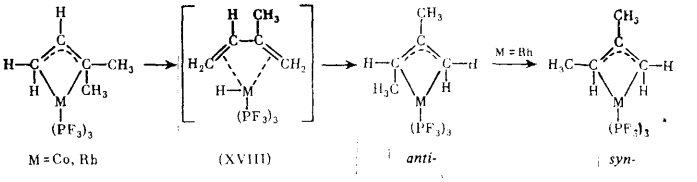
It follows from the data presented in Sections II–V that the order in which the diolefin combines with various reagents is determined by the sum of many factors. In contrast to the familiar characteristics, established for the addition of "classical" electrophiles and nucleophiles to diolefins[216–218], which is likely to have an ionic mechanism, the order of addition of transition metal derivatives

is independent of the direction of electron shifts induced in the molecules of these hydrocarbons under the influence of the electron-donating or electron-accepting substituents. The nature of the transition metal, its valence state, the number and nature of the ligands combined with the latter, the polarisation of the substrate molecule in the π-complex, and steric effects play the main role in the reactions which we have been considering. At the present level of our knowledge it is impossible to take into account all these factors in each specific case. However, there is one general very important characteristic of the reactions involving the insertion of diolefins in a transition metal–ligand bond: the addition reaction leads to the formation of only the *anti*-isomers of the π-allyl adducts; the *syn*-complexes are a result of the *anti*-*syn* isomerisation. This situation is illustrated by the examples in Table 9 and also by data obtained in the study of the mechanism of the hydrosilylation of 1,3-dienes under the influence of palladium, nickel, cobalt, and rhodium complexes [219-223].

Table 9. The configurations of the π-allyl ligand in the initial and final products of the addition of 1,3-diene to transition metal–ligand bonds.

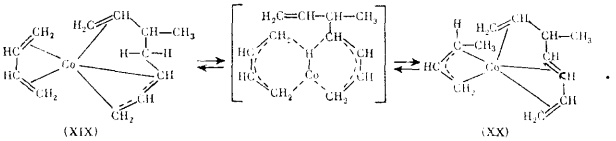
1,3-Diene	Initial transition metal compound	Configuration of π-allyl ligand		Refs.
		in initial compounds	in final products	
		π-Crotyl		
Butadiene	$HCo(CO)_4$	*anti*- and *syn*-	*syn*-(heating	11-13
Butadiene	$HCo(PF_3)[P(C_6H_5)_3]_3$	*anti*-	*syn*-(heating, addition of electron donors)	16
Butadiene	$CoCl_2 + Zn + P(C_6H_5)_3 + C_2H_5OH$	*anti*-	*syn*-	42,43
Butadiene	$HNi[P(OCH_3)_3]_4HSO_4$	*anti*-(88%) and *syn*-(12%)	*syn*-(95%) and *anti*-(5%) (70°C; 1.4 h)	18
Butadiene	$HFe(CO)_4SiCl_3$	*anti*-	*syn*-(heating)	9
Butadiene	$HPt(ClO_4)[P(C_6H_5)_3]_2$	*anti*-	*syn*-(heating)	34
Butadiene	$HPt(acetone)[P(C_6H_5)_3]_2 \cdot PF_6$	*anti*-	*syn*-(heating)	33,34
		1,3-Dimethyl-π-allyl		
Penta-1,3-diene	$HNi[P(OCH_3)_3]_4HSO_4$	*anti*, *syn*-(100%)	*syn*, *syn*-(80%) and *anti*, *syn*-(20%) (50°C; 0.4 h)	18
Penta-1,3-diene	$HCo(CO)_4$	*anti*, *syn*- and *syn*, *syn*-	*syn*, *syn*-	13
		1,2-Dimethyl-π-allyl		
Isoprene	$HNi[P(OCH_3)_3]_4HSO_4$	*anti*-(62%) and *syn*-(18%)	*syn*-(59%) and *anti*-(24%) (75°C; 0.9 h)	18
		1,2-Disubstituted π-allyl ligands		
Isoprene, 2-ethyl-2-isopropylbutadienes	$(C_4H_7NiI)_2$	*anti*-	*syn*- and *anti*- (heating)	14,16 155-160
2-t-Butylbutadiene	$(C_4H_7NiI)_2$	*anti*-	*anti*-	141,156 158-160

The formation of only the *anti*-isomers of the π-allyl adducts in the first stages of the insertion process suggests that in the transition state of the reaction there is always a *cis*-orientation of the diolefin molecule, which determines the stereoselectivity of the process. The relation between the *cis*-oriented 1,3-diene and the *cnti*-structure of the π-allyl ligand have been established experimentally. Consider, for example, the available data [26,88,89] for the skeletal isomerisation of the 1,1-dimethyl-π-allyl ligand to the 1,2-dimethyl-π-allyl ligand in the tris(trifluorophosphine) complexes of cobalt and rhodium. The proximity of the hydrogen atoms of the *anti*-methyl group in the 1,1-dimethyl-π-allyl complex to the metal permits the transfer of one of them to the metal with formation of the *cis*-dienemetal hydride complex (XVIII):



The migration of this hydrogen atom to the other end of the *cis*-oriented diene determines the ***anti***-structure of the 1,2-dimethyl-π-allyl complex.

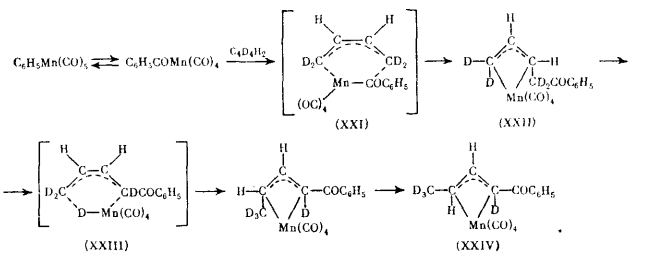
The ease of migration of hydrogen from the *anti*-methyl and *anti*-methylene groups is responsible for the existence of the complex having the general formula $CoC_{12}H_{19}$ in the form of two isomers, (XIX) and (XX), in equilibrium [39,40]. In this equilibrium the transition state is apparently a metallobicyclic complex:



It is easy to account similarly for the structure of the adduct of $C_6H_5Mn(CO)_5$ and butadiene [121] (Scheme 3).

Only the *cis*-orientation of the 1,3-diene in the transition stage (XXI) can lead to the complex (XXII) with deuterium atoms in the *anti*-substituent of the π-allyl ligand. The migration of the deuterium atom nearest to the metal atom via the transition state (XXIII) results in the skeletal isomerisation of the π-allyl ligand. The last reaction stage is the *anti*–*syn* isomerisation with formation of the observed product (XXIV).

Scheme 3

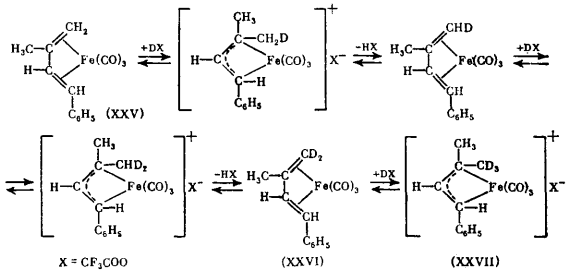


A clear demonstration of the genetic relation between the *cis*-structure of the coordinated diene and the *anti*-configuration of the substituent in the π-allyl complex formed is provided by data for the protonation of the diene complexes of iron [224-235], iridium [236], molybdenum [237,238], and cobalt [239]. For example, the cisoid form of the diene in the butadiene- and pentadiene-iron tricarbonyls is responsible for the selective formation of the *anti*-π-crotyl and *anti*,*syn*-1,3-dimethyl-π-allyl complexes [224,225].

The experimental data for the protonation of butadiene-iron tricarbonyl at low temperatures showed that, regardless of the nature of the protonating agent, the proton adds

exclusively to the *anti*-methyl group of the π-crotyliron complex[226]. Treatment of 3-methyl-1-phenylbutadiene-iron tricarbonyl (XXV) with deuterium chloride yielded a π-allyl complex containing deuterium only in the *anti*-methyl group[227]. In solution in CF_3COOD compound (XXV) undergoes a number of successive transformations leading to the diene complex (XXVI) and the π-allyl complex (XXVII) containing the perdeuteromethylene and *anti*-perdeuteromethyl groups:

Scheme 4

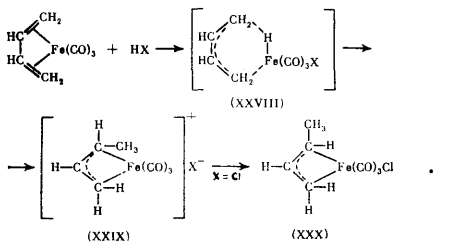


X = CF_3COO (XXVI) (XXVII)

The protonation and deprotonation reactions presented in Scheme 4 proceed via the intermediate hydridodieneiron complexes, whose existence has been demonstrated by a number of data[226,228-231].

The mechanism of the formation of π-allyl adducts, for example, from butadieneiron tricarbonyl and proton-containing acids, can be represented as follows:

Scheme 5

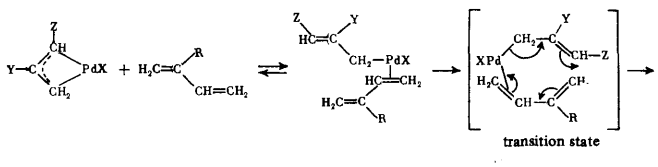


(XXVIII) (XXIX) (XXX)

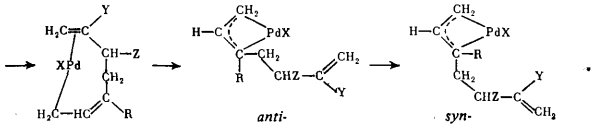
The first stage of the reaction is the oxidative addition of H–X to the initial zerovalent iron complex ($Fe^0 \rightarrow Fe^{2+}$). The *cis*-structure of the diene in the transition state, which precedes the insertion of the diene in the Fe–H bond in (XXVIII), is responsible for the exclusive formation of the *anti*-π-crotyl complex (XXIX) regardless of the nature of the anion of the Brønsted acid. However, if X = Cl, the latter enters the inner coordination sphere of the iron atom and promotes the rapid *anti*–*syn*-isomerisation of the π-crotyl ligand, giving rise to the observed *syn*-complex (XXX).[232,233] The metallocyclic transition state, analogous to compound (XXVIII), is apparently also responsible for the preferential formation of *cis*-σ-crotylmanganese pentacarbonyl when butadiene reacts with $HMn(CO)_5$.[4]

According to ideas put forward by Hughes and Powell[149], the products of the insertion of dienes in the allyl–palladium bond are formed via a metallocyclic transition state with a *cis*-oriented 1,3-diene. The new carbon–carbon bond then arises outside the coordination sphere of the palladium atom:

Scheme 6



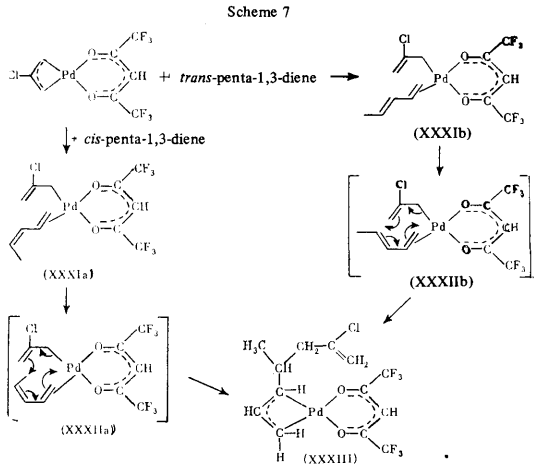
transition state



anti- *syn*-

The proposed mechanism agrees with the order in which π-allyl complexes of palladium add to conjugated dienes and also with the relative reactivity of the latter. For example, the structures of the intermediate π-complexes (XXXIa) and (XXXIb) (Scheme 7), formed on coordination of *cis*- and *trans*-penta-1,3-dienes, explain satisfactorily why the two dienes induce the *syn*–*anti* proton exchange in 2-chloro-π-allylpalladium hexafluoroacetylacetonate at virtually equal rates.

Scheme 7



(XXXIa) (XXXIIa) (XXXIb) (XXXIIb) (XXXIII)

In the transition state generated in the formation of the insertion product (XXXIII) the position of the methyl substituent in the *cis*-pentadiene (XXXIIa) is sterically less favourable than in the *trans*-pentadiene (XXXIIb). This is responsible for the much slower insertion of *cis*-penta-1,3-diene compared with the *trans*-isomer. This stereochemical requirement of a *cis*-planar structure of the diene before the insertion reaction resembles the behaviour of 1,3-dienes in Diels–Alder reactions[240-242].

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Thus, summarising the foregoing survey, one must conclude that the formation of *anti*-structures of the π-allyl products of the addition of 1,3-dienes to transition metal compounds is a kinetically controlled process. The subsequent reactions of the *anti*-complexes are determined by thermodynamic and steric factors. The knowledge of the exact chemical compositions of both the initial and final products of the reactions of 1,3-dienes with transition metal compounds is extremely important, since these complexes, involved in the addition reactions of subsequent 1,3-diene molecules, determine the microstructure of the monomeric units of the oligomeric or polymeric molecules formed.

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Application of Ion-exchange Resins in Photometry

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The application of ion-exchange resins in the spectroscopic method of studying complex compounds is discussed. The possible use of ion-exchange resins or poly(vinyl chloride) films impregnated with organic reagents in analytical practice with a photometric detector is examined. 82 references.

CONTENTS

I.	Introduction	774
II.	Study of complexes by ion-exchange resin spectroscopy	774
III.	Application of ion-exchange resin photometry in analytical practice	776
IV.	Methods of preparation of samples for analysis	778
V.	Possible future developments of ion-exchange resins in photometry	778

I. INTRODUCTION

The new comprehensive programmes of environmental protection have generated new requirements for methods of analytical control of natural waters and waste waters. The foremost needs are for sensitivity, reproducibility, speed, reliability, and demonstrable precision of the relevant measurement, together with the development of analytical methods which can be automated and whose results can be processed on a computer.

One approach to this problem is to develop new analytical procedures (and to improve existing ones) in which a method of detection is combined with an enrichment method. The spectroscopy of ion-exchange resins, in which the wanted element is concentrated in the resin phase before being directly estimated, is a promising example of the newer analytical procedures.

In 1954 Fujimoto[1] studied the colour changes of ion-exchange resins produced by the sorption of various ions: his results have been applied in the development of qualitative and semiquantitative methods of elemental analysis. The first spectrophotometric study of resins was reported by Ryan[2] in 1960. However the full potential of the spectrophotometry of resins as a practical method of quantitative analysis was only demonstrated in 1976 (by a group of Japanese workers[3]).

This review will deal with studies of the spectroscopy of ion-exchange resins in coordination chemistry and in analytical chemistry.

We shall not be concerned with the extensive researches on hydration phenomena which have relied on the spectroscopic characteristics of ion-exchange resins. Molecular interactions during hydration have been studied by i.r. spectroscopy by Zundel over many years, and they are discussed in his monograph[4]. The nature of complex hydrates in ion-exchange resins and the state of the water in these materials, studied by NMR spectroscopy, were recently reviewed by Bystrov and coworkers[5], and further discussion of these phenomena would be superfluous.

II. STUDY OF COMPLEXES BY ION-EXCHANGE RESIN SPECTROSCOPY

Ion-exchange resins are widely used in studies of complex formation to determine the composition and stability of the complexes[6]. Because of the difficulty of determining the composition of complexes sorbed by resins, and of the difference between the forms of the complex in solution and in the resin phase respectively, it is necessary to study the spectral characteristics of the resin phase. Ryan[2,7,8] examined the complex forms of tetravalent and hexavalent actinides sorbed by anion exchange resins. Neptunium, plutonium, and uranium compounds were identified by comparing the absorption spectra of the resins with those of aqueous or non-aqueous solutions of the complexes, and with the spectra of the complexes in the crystalline state. Data on the solubility of the complexes in the various media were required.

In the case of tetravalent actinides sorbed by anion exchange resins from hydrochloric or nitirc acid solutions the anion entering the resin phase is MX_6^{2-}, where M = Pu, Np, Th, U, and X = Cl^-, NO_3^-. We should note that these compounds are sorbed in the presence of both the salts (sodium chloride, calcium nitrate) and the acids of the ligands. On the other hand in an aqueous phase these compounds can exist only at high concentrations of nitric or hydrochloric acid. For example, MCl_6^{2-} (where M = Np, Pu, U) exists in 12 M HCl, $Pu(NO_3)_6^{2-}$ in 13 M HNO_3, $Np(NO_3)_6^{2-}$ in 14 M HNO_3, and $U(NO_3)_6^{2-}$ in 15.7 M HNO_3.

The following mechanism was proposed[2] for the formation and sorption of the complex anions in the resin:

$$M^{+m} + n\,X^{-y} \rightleftarrows MX_n^{-ny+m},$$

$$MX_n^{-ny+m} + \frac{ny-m}{y}\,X^{-y}\,(\text{res}) \rightleftarrows MX_n^{-ny+m}\,(\text{res}) + \frac{ny-m}{y}\,X^{-y},$$

$$MX_n^{-ny+m} + (ny-m)\,H^+ \rightleftarrows H_{ny-m}MX_n.$$

The suggested reactions satisfactorily explain various phenomena observed during the sorption of metal anions by ion-exchange resins: the increased sorption in the presence of acids, the maximum in the curve of distribution coefficient against ligand concentration, and the possible sorption of intermediates formed during the reaction[2].

In the case of the formation of hexavalent actinide complexes in the resin phase the compounds $MO_2(NO_3)_4^{2-}$ and $MO_2(NO_3)_3^-$ are detected, whereas in an aqueous phase the concentration of actinide tetranitrates is very small, and in concentrated nitric acid only $MO_2(NO_3)_3^-$ is formed[7]. The relative concentration of these complex anions in the resin phase is found to be independent of the composition of the aqueous phase, but determined by the properties of the resin (total sorption capacity, extent of saturation by nitrate ions). Before this work it has been generally assumed that the ions entering the resin phase are those already present in solution. Only by using a spectrophotometric method could the difference between the compounds in the two phases be demonstrated. The identification of the actinide tetranitrates in the resin phase relied on the determination of the

charge of the sorbed compounds, on the synthesis of various complexes, and on comparative studies of the optical properties of complexes in the resin phase and in the crystalline state[7].

The sorption of uranyl ions has been studied for fluoride, chloride, bromide, and sulphate systems as well as for nitrate systems[9,10]. Spectrophotometric studies of cation and anion exchange resins after sorption of uranyl compounds gave extensive information on complex formation by the uranyl ion with these ligands, and identified the products of multi-step complex formation reactions (by utilising the selective sorption properties of the resin as a function of resin type and of the nature of the solvent).

The ions UO_2Cl^+ and UO_2Br^+ (identified by their characteristic absorption spectra in the region of stretching vibrations of the U–O bond) are sorbed by the resin from chloride and bromide systems at low concentrations of the halide ion. Fluoride cannot form a positively charged complex with the uranyl ion. Even at very low concentrations of F^- the equilibrium is displaced towards the formation of anionic fluorine complexes. Thus a study of the sorption of halogen complexes of uranyl on a cation exchanger established the following stability sequence of the anionic uranyl complexes with halide ions[9]:

$$F^- > Cl^- > Br^-.$$

The compounds $UO_2F_3^-$, $UO_2Cl_3^-$, $UO_2Cl_4^{2-}$, and $UO_2Br_4^{2-}$ were identified[9] from the visible and i.r. absorption spectra of anion exchange resins after sorption of complex uranyl ions. The coordination numbers and the symmetry of the intermediates were obtained by analysing the spectral characteristics. Thus the $[UO_2X(H_2O)_5]^+$ complexes have a coordination number of 6 and a D_{3h} point-group symmetry. Increasing the number of halogen groups ($UO_2X_3^-$, $UO_2X_4^{2-}$) lowers the coordination number to 4 (D_{4h} point-group symmetry).

Spectroscopic studies of resins used in the sorption of uranyl compounds in the presence of sulphate[10] confirmed the presence of consecutive reactions during the complex formation between uranyl and sulphate. The following compounds were identified: $UO_2HSO_4^+$, $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$. It was shown that the ion $[UO_2(H_2O)_6]^{2+}$ is sorbed by a cation exchanger from a solution of uranyl sulphate in the absence of an excess of SO_4^{2-} ions. Increasing the concentration of sulphuric acid in the system causes the ion $UO_2HSO_4^+$ to be sorbed by the cation exchanger, whereas in neutral sulphate solutions this ion is not detected. The following compounds were also detected: $UO_2(SO_4)_2^{2-}$ (sorption from solutions containing uranyl sulphate with or without an excess of sulphuric acid) and $UO_2(SO_4)_3^{4-}$ (sorption from solutions containing an excess of lithium sulphate). The force constants f and the radii of UO_2^{2+} were calculated[10] from the U–O stretching vibration frequencies in the i.r. spectra (see Table 1). We note that the replacement of water molecules by SO_4^{2-} groups increases the radius of the UO_2^{2+} ion from 1.719 to 1.740 Å, indicating a change in the nature of the bond during the transition from the hydrated UO_2^{2+} ion to the $UO_2(SO_4)_3^{4-}$ anion.

Choppin and coworkers[11] studied the visible and i.r. absorption spectra of neodymium complexes with various ligands (SCN^-, Cl^-, NO_3^-, NO_2^-, CO_3^{2-}, OCN^-, CH_3COO^-, EDTA) and concluded that the spectra of the ion-exchange resins after sorption of these anionic neodymium complexes are almost indistinguishable from those of the concentrated aqueous solutions.

Most of the reported spectroscopic investigations of complexes sorbed by resins have been concerned with the ions of transition metals such as cobalt, nickel, copper, and iron[12–31]. This work is important not only because it adds to our understanding of the complex formation processes, but also because it highlights possible applications of ion-exchange resins as vehicles for the sample to be analysed by spectroscopic methods, since the formation of complexes by transition-metal ions in aqueous and in non-aqueous media is now well understood. By comparing results for ion-exchange resins containing the sorbed copper cations $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_5Cl]^+$, and the anions $[CuCl_3(H_2O)]^-$ and $[CuCl_4]^{2-}$, the authors conclude[12,13] that ion-exchange resins are suitable matrices for the measurement of absorption and ESR spectra.

Table 1. Quantitative characteristics of uranyl compounds formed in a sulphate solution.

Compound	Resin	ν_3, cm^{-1}	f	$R_{UO_2^{2+}}$, Å
$UO_2(H_2O)_6^{2+}$	Dowex-50	958	7.625	1.719
$UO_2HSO_4^+$	Dowex-50	950	7.466	1.722
$UO_2(SO_4)_2^{2-}$	Dowex-1	910	6.880	1.738
$UO_2(SO_4)_3^{4-}$	Dowex-1	905	6.805	1.740

Marov and coworkers[14] studied the sorption of the copper cations $[Cu(H_2O)_6]^{2+}$ by a weakly basic anion exchanger containing primary, secondary, and tertiary amino groups, and they explained it in terms of complex formation between Cu(II) and the anion exchanger. This interpretation was confirmed by the ESR spectra. The following mechanism was proposed[14] (in the case of the primary groups) for the interaction between the copper cations and the anion exchanger:

$$4RNH_2 \ldots HOH + [Cu(H_2O)_6]^{2+} \rightarrow [Cu(RNH_2)_4(H_2O)_2]^{2+}.$$

These results are fully consistent with earlier ESR work[15] on the structure of a copper complex sorbed by a weakly basic anion exchanger.

Japanese workers[16] have reported the formation of anionic copper complexes during sorption by anion exchangers, and they have shown that the resins can be used in spectrophotometric studies. They examined the changes in the absorption spectra of the resins (broadening of the absorption peak, extending over the region $\lambda = 400–500$ nm) which occur as the concentration of copper ions in the system is increased. Whereas Heitner-Wirguin and Cohen[12] ascribe this phenomenon to changes in the structure of the sorbed anion (transition from $CuCl_4^{2-}$ to $CuCl_3^-$), these workers[16] assume dimerisation of the copper anions in the resin in contact with a more concentrated solution of copper chloride:

$$2CuCl_3^- + Cl^- \rightleftarrows \left[\begin{array}{cccc} & Cl & Cl & \\ & | & | & \\ Cl-Cu & -Cl- & Cu & -Cl \\ & | & | & \\ & Cl & Cl & \end{array}\right]^{3-}.$$

The formation of $Cu_2Cl_7^{3-}$ was confirmed[16] by applying the previously reported method[17–19] of determining the composition of the complex sorbed by a resin from the distribution coefficient. The quantity $\bar{n}_R$ (the mean

number of ligands in the metal complex within the resin phase) is determined from a plot of $\{\lg D + (\bar{n} - m/l)\lg[L]\}$ against $\lg[L]_R$, where D is the distribution coefficient of the metal M, $\bar{n}$ is the mean number of ligands in the complex, l is the charge on the anion of the ligand, and the subscript R refers to the resin phase. The basic equation for calculating $\bar{n}_R$ can be written

$$\frac{d\{\lg D + (\bar{n} - m/l)\lg[L]\}}{d\lg[L]_R} = \bar{n}_R - \frac{m}{l}.$$

The validity of this method of determining the number of ligands in the complex was tested with the well characterised iron(III)–chloride and cobalt(II)–chloride systems. The final conclusion was that the ion $CuCl_3^-$ is present in an anion exchange resin phase, but an increase in the concentration of copper ions in hydrochloric acid solution leads to the formation of $Cu_2Cl_7^{3-}$ ions.

Waki and coworkers[20] used this method to calculate the stability constants of polyphosphate copper complexes formed in an ammoniacal solution (pH > 10.5) by the reaction

$$Cu(NH_3)_4^{2+} + P_nO_{3n+1}^{(n+2)-} \rightleftarrows Cu(NH_3)_3P_nO_{3n+1}^{n-} + NH_3$$

The following stability sequence of the copper complexes with polyphosphates was established:

$$P_2 > P_3 > P_1 .$$

The difference in the absorption spectra of the resin phase was consistent with the assumed differences in structure.

Rutner[21] has analysed the reflectance spectra of anion exchange resins containing Co(II) and Fe(III) complexes sorbed from chloride solutions. The reflectance spectra of the cobalt complexes have minima at 695, 665, and 635 nm, corresponding to the absorption bands of the $CoCl_4^{2-}$ complex which is formed in the aqueous phase in the presence of 7.25 M HCl. The spectrum of the Fe(III) complex shows a single peak at 362 nm, corresponding to the absorption maximum of the $FeCl_4^-$ complex anion in aqueous solution.

The halogen complexes of cobalt and nickel were studied by Nortia[22], who also concluded that the compounds sorbed by the anion exchanger have the composition MX_4^{2-} (where $M^{2+} = Co^{2+}$, Ni^{2+}, and $X^- = Cl^-$, Br^-, and I^-). He examined[22] the reflectance spectra of the halogen complexes of cobalt and nickel in the resin phase, and he showed that ion-exchange resins can be used as solid solvents for measuring the magnetic moments of these complexes.

Coleman's study[23] of the chloride complexes of cobalt on ion exchangers was conducted at constant concentration of the metal in the resin, which was treated after sorption with gaseous HCl–H_2O mixtures of different component ratio. He showed that the configuration of the complex changes from octahedral to tetrahedral as the concentration of Cl^- increases. The identification of the $CoCl_4^{2-}$ ion in the anion exchanger from spectrophotometric measurements confirms earlier results[21,22].

The coordinational configuration of the cation of an element in the resin phase has attracted a great deal of interest[24-26]. Thus it was shown that Co, Ni, and Cu exist as hydrated ions in a sulphonated cation exchanger saturated with water. On drying the resin (by heating it to 100°C) the i. r. spectra show a decrease in the number of hydrated metal complexes and a corresponding increase in the intensity of the spectral bands arising from the interaction of the metal ions with the sulphonic acid groups of the resin. In contrast to the sulphonated resins, in the case of carboxylic acid resins the metal ions interact with the carboxylic acid groups even in the moist resin[25]. This is consistent with the known relative complexing powers of malonic acid (the monomer of the carboxylic acid resin used in the investigation) and of water.

A series of papers by Heitner-Wirguin and Ben-Zwi[27-31] discusses the Co(II)–X^- system, where $X^- = Cl^-$, NO_3^-, and SCN^-, and identifies the successive steps of the complex formation reaction ($Co(H_2O)_6^{2+}$, $Co(H_2O)_5X^+$, $Co(H_2O)X_3^-$, and CoX_4^{2-}). The cobalt–chloride system was studied in both aqueous and non-aqueous solutions: acetone and ethanol were used as solvents because they form a solvation shell similar to that formed by H_2O in aqueous solutions of the cobalt complex.

III. APPLICATION OF ION-EXCHANGE RESIN PHOTOMETRY IN ANALYTICAL PRACTICE

The changes in optical properties of resins during the sorption of ions were first exploited by a group of Japanese workers[32-34] in the 1950's. The colour changes during the reaction are an indication of the presence of various ions, and they can be used very successfully in qualitative spot tests. Furthermore the depth of colour, estimated visually against a reference scale of standard colours, offers a semiquantitative method of analysis of various ions. Therefore the work on spot tests with resins deserves to be mentioned as the earliest example of the application of resin photometry in analytical chemistry. Qualitative drop tests for various elements, leading to the formation of coloured complexes, chelate compounds, and dyes, are listed in Table 2.

A change in colour may be due also to the formation of a precipitate at the phase boundary[66-68], or to catalytic reactions[69]. Fujimoto[70] proposed the addition of an organic solvent (immiscible with water) after complex formation and sorption. In this case the colour change can be obseved without separating the phases.

Drop reactions on resins can be carried out by two fundamentally different methods[71]: 1) the formation of a coloured compound which is subsequently taken up by the resin phase, and 2) prior impregnation of the resin with the reagent, so that the reaction between the ion to be determined and the reagent occurs within the resin phase. Detailed information on experimental procedure and on the advantages of qualitative drop reactions on resins can be found in a review by Fujimoto[72] and in textbooks[73,74].

A sensitive new photometric method of determining various elements in natural waters, based on the direct measurement of light absorption in an ion-exchange resin containing sorbed ions, was proposed in 1976 by Yoshimura and coworkers[3]. The determination relies on the colour reactions of Cr(VI) with diphenylcarbazide, of Fe(II) with 1,10-phenanthroline, of Cu(II) with Zincon, and of Cd(II) with thiocyanate. These workers[3] only used standard analytical reactions, which they combined with measurements of light absorption by an ion-exchange resin. The sensitivity of this method is more than 10 times greater than that of the direct spectrophotometric method. Table 3 lists some comparative data on the sensitivity of photometric analysis in ion-exchange resins and in aqueous solutions[3]. The measurement error is 5–10%

An improved method of determination of Cr(VI) by the reaction with diphenylcarbazide, using ion-exchange resin photometry, has been described[75]: up to 1 mg litre^{-1} of Cr can be determined in natural waters by using the recommended procedure.

Fujimoto's method of impregnating the resin with the reagent[71] consists in replacing the mobile counter-ions of the polymer network (containing chemically bound ions) by ions of the organic reagent. When the resin is placed in contact with the ions to be determined the latter penetrate into the resin phase where they form the corresponding coloured complexes.

Table 2. Drop reactions on resins.

Element	Reagent	Resin*	Limit of detection, μg	Dilution limit	Refs.
Al(III)	Alizarin	III	0.08	—	32
B	Curcumin	II	0.06	$1:5\cdot10^6$	33
Bi(III)	thiourea	V	0.1	$1:4\cdot10^5$	34
Bi(III)	Pyrocatechol Violet	IV	0.03	$1:13\cdot10^5$	35
$Br^-(Br_2)$	Schiff's reagent	VII	1.2	$1:10^4$	36
Co(II)	NH_4SCN	II	0.16	$1:13\cdot10^4$	1
Co(II)	nitroso-R-salt	I	0.003	$1:14\cdot10^6$	37
Cr(III), Cr(IV)	H_2O_2	I, II	0.3	$1:10^5$	38
Cu(II)	*p*-phenylenediamine and NH_4SCN	I	0.02	$1:2\cdot10^6$	39
Cu(I), Cu(II)	Bathocuproindisulphonic acid disodium salt	IV	0.001	$1:3\cdot10^7$	40
Cu(II)	Calcion	IV	0.003	$1:10^7$	40
Cu(II)	colour of copper ion, pH 5.0	VIII	0.1	$1:4\cdot10^5$	41
Fe(III)	Tiron	I	0.008	$1:5\cdot10^6$	43
Fe(III)	sulphosalicylic acid	I	0.004	$1:10^6$	43
Fe(III)	chromotropic acid	I	0.02	$1:2\cdot10^6$	43
Fe(II), Fe(III)	α,α′-dipyridyl	IV	0.0025	$1:16\cdot10^6$	44
Fe(III)	Ferroin	I	0.004	$1:12.5\cdot10^6$	45
Ga(III)	Alizarin S	I	0.03	$1:10^6$	46
Ge(IV)	hematoxylin	III	0.003	$1:2\cdot10^7$	47–49
Hg(II)	diphenylcarbazone	I	0.1	$1:10^4$	50
In(III)	Alizarin S	II	0.03	$1:13\cdot10^5$	51
Mg(II)	Xylidene Blue	I	0.007	$1:15\cdot10^5$	52
Mo(VI)	NH_4SCN and $SnCl_2$	I	0.024	$1:16\cdot10^5$	53
Mo(VI)	hydrazine dihydrochloride and Methylene Blue	IV	0.001	$1:6\cdot10^7$	54
Ni(II)	dimethylglyoxime and Br_2	I	0.011	$1:38\cdot10^5$	55
Ni(II)	rubeanic acid	IV	0.021	$1:19\cdot10^6$	56
NO_2^-	*m*-phenylenediamine	IV	0.015	$1:29\cdot10^5$	57
NO_3^-	*m*-phenylenediamine and Zn	IV	0.08	$1:5\cdot10^5$	57
S^{2-}	*p*-aminodimethylaniline	VII	0.05	$1:8\cdot10^5$	58
Th(IV)	Alizarin S	III	0.03	$1:10^6$	59
Ti(IV)	H_2O_2	IV	0.25	$1:16\cdot10^4$	60
Ti(IV)	Tiron	I	0.026	$1:11\cdot10^5$	61
Tl(I)	I^-	III	0.01	$1:13\cdot10^5$	62
V(V)	8-hydroxyquinoline	VIII	0.025	$1:16\cdot10^6$	63
V(V)	H_3PO_4 and Na_2WO_4	I	0.2	$1:2\cdot10^5$	63
V(V), Fe(III)	α,α′-dipyridyl	IV	0.1	$1:4\cdot10^5$	63
V(V)	diphenylamine	IV	0.04	$1:10^6$	53
Zr(IV)	Alizarin S	I	0.03	$1:13\cdot10^5$	64
Zr(IV)	Pyrocatechol Violet	IV	0.01	$1:4\cdot10^6$	65

*Symbols: I) strongly basic anion exchanger, 1%DVB; II) strongly basic anion exchanger, 8%DVB; III) strongly basic anion exchanger impregnated with reagent, 1%DVB; IV) strongly acidic cation exchanger, 1%DVB; V) strongly acidic cation exchanger, 2.5%DVB; VI) strongly acidic cation exchanger, 8%DVB; VII) strongly acidic cation exchanger impregnated with reagent, 8%DVB; VIII) carboxylic acid cation exchanger, 1%DVB.

Tanaka and coworkers[76,77] suggested the use of transparent polymer films based on poly(vinyl chloride) (PVC) to determine various metal ions. They examined[76] the possibility of determining copper, zinc, cadmium, nickel, mercury, and manganese by using PVC membranes impregnated with 1-(2-pyridylazo)-2-naphthol (PAN). Some analytical characteristics of PVC membranes[76] after contact with solutions of these ions are given in Table 4. The optical density was shown to be proportional to the concentration of the metal being determined in the range 10^{-5}–10^{-4} M. Because the absorption by the membrane itself is negligible in the region of absorption by the complexes (550–570 nm) it is legitimate to measure the absorption of the membrane with respect to that of air.

Table 3. Relative sensitivity of the photometric analysis of ion-exchange resins (c_1) and of solutions (c_2). (The quoted figures are the metal concentrations giving an optical density $A = 0.50$.)

Element	$10^6 c_1$, M	$10^5 c_2$, M
Cr(VI) *	0.6	1.8
Cr(VI) **	0.6	1.8
Fe(II)	2.9	3.9
Cu(II)	2.5	2.2
Co(II)	9.4	3.0

* In $0.05N$ H_2SO_4
** In $0.05N$ H_2SO_4 + 0.6 M NaCl

Table 4. Analytical characteristic of PVC membranes.

Ion	λ_{max}, nm
Cu^{2+}	565
Zn^{2+}	558
Cd^{2+}	558
Ni^{2+}	574
Hg^{2+}*	565
Mn^{2+}*	565

*Glycine + NaOH buffer solution; in the other cases NH_4Cl + NH_4OH (pH ~ 10).

A PVC membrane impregnated with bathophenanthroline has been used[77] for the rapid semiquantitative determination of iron in water. Because the reaction between Fe(II) and bathophenanthroline (Bphen) gives the charged complex $Fe(Bphen)_3^{2+}$, the PVC membrane was additionally impregnated with tributyl phosphate. It was shown that the colour developed by the membrane has an absorption peak at $\lambda = 540$ nm. The optimum concentration of hydrogen ions is in the range pH 3–6 (0.1 M acetate buffer). The optical density of the membrane depends on the time of contact between the phases: as Fig.1 shows, the optical density for a contact time of 20 min is significantly higher than for a contact time of 5 min. It is important to note that the optical density remains constant for a long period. The light absorption of the membrane is affected also by the nature of the anion present in solution. For a total anion concentration of 2×10^{-2} M the effect of the anion on the colour of a membrane in contact with a solution of Fe(II) increases in the sequence

$$Cl^- < Br^- < I^- < ClO_4^- < \text{alkylbenzoylsulphonate}.$$

Metal ions which form coloured complexes with Bphen (copper, cobalt, nickel, manganese) interfere with the determination of iron in solutions by a PVC membrane

impregnated with Bphen and tributyl phosphate. Alkali and alkaline earth metals, aluminium, and also the anions sulphate, phosphate, chloride, and nitrate have practically no effect on the determination of Fe(II).

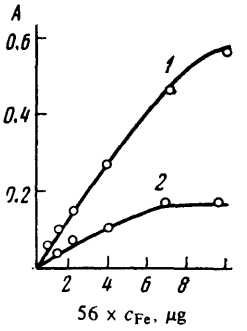


Figure 1. Calibration curves for the determination of iron: contact time 20 min (*1*) and 5 min (*2*).

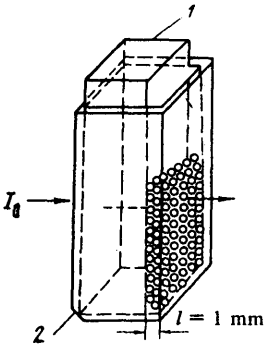


Figure 2. Conventional form of the cell for photometric analysis of the resin: *1*) quartz insert, *2*) drainage hole.

IV. METHODS OF PREPARATION OF SAMPLES FOR ANALYSIS

There are several methods of preparing the sample for photometric analysis (i.e. of preparing a light-absorbing layer uniformly packed with the ion-exchange resin). As in the photometric method of analysis of solutions, one uses quartz cells with parallel walls filled with resin grains[2,3,7,8,11,16,27]. Light absorption is measured 15–20 min after addition of the resin (the time needed to form a uniformly packed layer). In order to obtain the maximum packing density (and thus ensure reproducible results) it may be desirable to use a centrifuge[11,27].

Trace amounts of chromium in natural waters have been determined[75] in a cell with an outlet at the bottom: this allows the solution between the resin grains to be drained away, and helps the formation of a densely packed layer. A common form of the cell is shown in Fig.2. A quartz insert is used to decrease the thickness of the measured layer[8,16,75].

In the quantitative determination of elements[3] corrections must be applied for the light absorbed by the resin, the reagent, and the solution between the grains:

$$A' = A_{meas} - A_{sol} - A_{res} - A_{reag}.$$

Spectral measurements can be made with a mixture of the resin and colourless petroleum jelly, which is either added to the cell[24] or uniformly smeared on a glass plate[20]. Coleman[23] described a method of pressing the resin granules into disks, which are then used for sorption experiments and for light-absorption measurements. These disks are 0.2–0.6 mm thick.

A method of grinding the resin and pressing a mixture of the powdered resin with potassium bromide (or with petroleum jelly) has been used for i.r. spectral measurements[78-82]. Poly(vinyl chloride) membranes impregnated with an organic reagent were prepared [76,77] by dissolving PVC powder, a known weight of the reagent, and the required amount of plasticiser in tetrahydrofuran. After removing the solvent by evaporation the layer was placed between steel plates and pressed in a vacuum at 90°C. There is no information on the effect of lengthy storage on the analytical properties of the membrane.

V. POSSIBLE FUTURE DEVELOPMENTS OF ION-EXCHANGE RESINS IN PHOTOMETRY

The work discussed in this review suggests possible future developments of this area of analytical chemistry. First of all it should be possible to vary several parameters in order to achieve selectivity while increasing still further the sensitivity of the method, taking advantage of the concentration of the coloured complex which the resin offers. Furthermore the fund of knowledge available in the literature on the selectivity and sensitivity of reactions between metal ions and organic reagents still remains to be exploited.

Thus we envisage two main directions for further development, differing in the method used to produce the coloured complex in the resin.

1. The coloured resin is produced by allowing the metal ion to react with the anion of an organic reagent already present in the resin as an impregnant:

$$\text{R—X}^-\text{(res)} + \text{A}^- \rightleftarrows \text{R—A}^-\text{(res)} + \text{X}^-,$$
$$n\text{-R—A}^-\text{(res)} + \text{M}^{n+} \rightleftarrows \text{M(A—R)}_n\text{(res)}.$$

2. The coloured resin is produced by sorption of the complex formed by an organic reagent with the metal ion in the aqueous phase:

$$M^{n+} + m\,HA \rightleftarrows MA_m^{-(m-n)} + m\,H^+,$$
$$R\text{—}X^-\text{(res)} + MA_m^{-(m-n)} \rightleftarrows R_{(m-n)}\text{(res)}\,(MA_m) + (m-n)\,X^-.$$

Each approach has its own specific features and limitations. When further improvements in spectrophotometric apparatus and techniques are introduced, and the existing measurement problems are resolved, we can expect this combined method to be widely adopted in analytical practice for the determination of metal ions in natural waters and in waste waters.

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Diffusion of Electrolytes in Polymers

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The quantitative aspects of the diffusion of electrolytes in polymers are discussed. Methods of studying diffusion are reviewed. The transport of electrolytes in hydrophilic and in hydrophobic non-ion-exchange polymers is analysed. 179 references.

CONTENTS

I. Introduction 781
II. Characteristics of the diffusion of electrolytes in polymers 781
III. Methods of investigation 782
IV. Hydrophilic polymers 785
V. Hydrophobic polymers 790

I. INTRODUCTION

The diffusion of electrolytes in polymers has attracted a great deal of attention in recent years because of the theoretical and practical importance of this phenomenon. The prediction of the protective properties of polymer coatings, the permeability of biological membranes and tissues, dialysis in medicine, the desalination of sea water, the purification of sewer waters: all this is only a partial list of the processes in which diffusion plays a crucial role. Furthermore we can establish the mechanism of the degradation of polymers in aggressive media (solutions of electrolytes) only if we know the diffusion parameters and the state of the aggressive medium, i.e. the degree of dissociation and of interaction of the components of the electrolyte solution with the macromolecules and with the water molecules.

The theory used to discuss the diffusional transport of electrolytes treats diffusion systems as quasi-binary. However we must make allowance for a number of factors which are characteristic of the diffusion of electrolytes though they are irrelevant to other diffusants: dissociation into ions, hydration, interaction of flows, etc. A proper understanding of these factors is the main objective of current research on the quantitative description of the diffusion of acids, bases, and salts in polymers.

II. CHARACTERISTICS OF THE DIFFUSION OF ELECTROLYTES IN POLYMERS

1. The Presence of Ions

Electrolytes in a polymeric matrix can dissociate into ions which (unlike neutral particles) can move under the influence of a gradient in electrochemical potential. There are three main approaches to the description of the diffusional transport of electrolytes in polymers: the Nernst–Planck electro-diffusion equations[1,2], the thermodynamics of irreversible processes[3], and the theory of absolute reaction rates[4,5]. In spite of some differences in the description of the transport process (mainly, the treatment of the membrane as a heterogeneous matrix in the theory of absolute rates and the allowance for the interaction of the diffusion flows in the irreversible theory) all these approaches give mutually consistent results.

By definition, a flow of ions of a given kind (J_i) can be expressed as

$$J_i = u_i c_i A_i, \tag{1}$$

where u_i is the mobility of the ion (referred to unit force), c_i is its concentration in the polymer, and A_i is the generalised driving force of the transport process. Combining Eqn. (1) with the Nernst–Einstein expression for the electrochemical potential

$$D_i = u_i RT \tag{2}$$

and equating concentrations to activities we arrive at the basic Nernst–Planck equation for the diffusion of ions

$$J_i = -D_i c_i \left[\frac{1}{c_i}\frac{dc_i}{dx} + \frac{\bar{V}_i}{RT}\frac{dp}{dx} + \frac{z_i F}{RT}\frac{d\psi}{dx} \right]; \tag{3}$$

where $\bar{V}_i$ is the partial molar volume of the ion i, z_i is its charge, dp/dx and $d\psi/dx$ are the pressure gradient and the gradient of diffusion potential in the membrane respectively, T is temperature, R and F are the gas constant and the Faraday respectively.

In the absence of mobile or fixed charges, and of pressure gradients, Eqn. (3) is equivalent to the formulation of Fick's first law for a binary system of non-electrolytes. In the case of multicomponent diffusion a system of equations of type (3) can be solved by introducing the electroneutrality condition in the absence of electric current and of pressure gradients. In the simplest case (diffusion of a 1–1 fully dissociated electrolyte) the diffusion coefficient (D_{AC}) and the gradient of diffusion potential are given by

$$D_{AC} = \frac{D_A D_C}{D_A + D_C}; \quad \frac{d\psi}{dx} = -\frac{RT}{F}\left(\frac{u_C - u_A}{u_C + u_A}\right), \tag{4}$$

where D_i and u_i are the diffusion coefficient and the mobility of the cation (C) and of the anion (A) in the polymer. The diffusion coefficient of a partially dissociated electrolyte can be expressed as

$$D = [\alpha D_{AC} + 2(1-\alpha) D_n]\left(1 + \frac{d\ln y_\pm}{d\ln c}\right), \tag{5}$$

where α is the degree of dissociation of the electrolyte in the polymer, D_n is the diffusion coefficient of the neutral molecule, $y_\pm$ is the activity coefficient of the electrolyte, and c is the concentration of electrolyte in the polymer[6].

2. Allowance for Several Components

Experimental data for n-component diffusion systems show that each of the independent diffusion flows is a linear function of all the independent concentration gradients. According to the Gibbs–Duhem equation we can have $n - 1$ independent concentration gradients in such a system, giving rise to an equal number of diffusion flows. A full treatment of diffusion by irreversible thermodynamics involves the determination of $(n - 1)^2$ diffusion coefficients, which is a difficult experimental problem.

However in the diffusion of electrolytes the number of freely moving particles (N_0) is not necessarily equal to the number of components: it is given by the expression

$$N_0 = H + n_i - R_0 - 1, \quad (6)$$

where H is the number of types of independently mobile neutral molecules (including water, polymer, etc.), equal to the difference between the total number of types of uncharged molecules and the number of possible reactions between them, n_i is the number of electrolyte ions, and R_0 is the number of ionic reactions[3].

In order to satisfy the Onsager relation[7], which postulates equality of the cross diffusion coefficients, the number of independent D_i coefficients describing the diffusion of N_0 independently moving components must be decreased to

$$D_i = \frac{1}{2} N_0 (N_0 - 1). \quad (7)$$

The determination of a large number of diffusion coefficients in a multicomponent system requires a great deal of diffusion and thermodynamic information, which is seldom available. We usually have to rely on various simplifying assumptions on the relationship between the various diffusion coefficients and on the distribution of component concentrations in the system (see, for example, Refs. 7–9). Multicomponent diffusion is described most exactly by the Stefan–Maxwell equations, which are applied to transport phenomena in gases[10]. In biological systems and in reverse osmosis experiments diffusion is usually described by the Kedem–Katchalsky equations[10,11].

3. Choice of a Characteristic Diffusion System

The overall flow of any diffusing component with respect to an arbitrary system of coordinates (J_{0i}) can be expressed as the sum of a convective flow, due to the motion of the system as a whole with velocity w_s, and a true diffusion flow, measured relatively to the convective flow:

$$J_{0i} = w_s c_i + J_i. \quad (8)$$

The choice of a characteristic velocity depends on the properties of the system and on the method of investigation. The following characteristic systems are most commonly used: the Fick characteristic system, based on measurements of the mean volume velocity, 2) the Hittorf characteristic system, based on measuring the velocity of any one component (for example, the solvent) in the membrane, 3) the centre of mass characteristic system, based on measuring the velocity of the centre of mass, and 4) the lattice characteristic system, based on measuring the rate of displacement of the lattice sites in the crystal. The relationship between the flows and the diffusion coefficients in the various systems is discussed in detail in Ref. 3 (p. 239) and in Ref. 12.

4. Effect of an Unstirred Layer of Electrolyte Solution

When an electrolyte is diffusing in a polymer we often have to consider the effect of a liquid film of solution in contact with the polymer surface and adhering to that surface even when the system is stirred. This immobile layer, called the Nernst layer (see Ref. 2, p. 129), is found in all multicomponent systems. Allowance for the retardation of diffusion near the polymer surface is essential in the case of hydrophilic polymers with a high water content.

The criteria which determine whether the fixed layer can be ignored are discussed by Helfferich[13]. The transport of solute through a polymer membrane in the presence of a Nernst layer is described by the equation

$$J = -Dc\left[l\left(1 + \frac{2cl_N D}{D_N c_N l}\right)\right]^{-1}, \quad (9)$$

where l_N is the thickness of the Nernst layer, l is the thickness of the polymer, and the parameters with the subscript N refer to the solution in which the polymer is immersed. It follows from Eqn. (9) that for $D_N c_N l \gg Dcl_N$ the diffusion process is controlled by the polymer membrane, and for $Dcl_N \gg D_N c_N l$ the Nernst layer is rate-limiting.

The measurement of the thickness of the fixed layer is a difficult experimental problem. Peterson and Gregor[14] have calculated l_N as a function of the stirring rate by combining Eqn. (9) with indirect kinetic measurements. They found that l_N decreases by more than an order of magnitude as the stirring rate is increased. Other methods of measuring the thickness of the liquid layer include a new procedure[15] based on the current–voltage characteristics of the membrane. Measurements of l_N for spherical samples are described in Ref. 16.

5. Interaction Between the Electrolyte and the Polymer

If the polymer contains inorganic groups, strong interactions can occur between these groups and the diffusing electrolytes. A typical example of this behaviour is found in the aqueous electrolyte–polyamide system, discussed below. In polymers which are practically free from polar groups (polyethylene, polypropylene) the interactions between the diffusing components are predominant.

At present there is no general quantitative theory relating the structural parameters of the polymer to the diffusion coefficients of electrolytes within that polymer. An analysis of the diffusion of various electrolytes suggests that polymers can conveniently be classified into three groups according to their water content: polymers which easily dissolve water (> 10 wt.%), polymers in which the solubility of water is limited, and polymers which dissolve very little water (< 1 wt.%). The polymers of the first group are hydrophilic, the others are hydrophobic.

III. METHODS OF INVESTIGATION

1. Methods Based on Measuring the Permeability of the Polymer

The determination of diffusion parameters by measuring permeability consists in measuring the amount of electrolyte transported in unit time through unit area of the polymer film. The diffusion coefficients can be calculated

from data on the rate of transport under steady-state conditions and on the solubility of the electrolyte in the polymer by integrating Fick's equation

$$\bar{D} = q(c_0)\, l/(c_0 - c_p), \qquad (10)$$

where $\bar{D}$ is the integral diffusion coefficient[17], $q(c_0)$ is the rate of transport, and c_0 and c_p are the concentrations of electrolyte in the surface layer of the polymer on the side of the diffusion source (usually assumed to be equal to the solubility in the polymer) and on the side of the detector cell respectively. Under most experimental conditions $c_0 \gg c_p$, which simplifies Eqn. (10). We should note that the calculation of diffusion coefficients by this equation can lead to low values because the quantity c_0 as determined from solubility measurements includes both mobile and immobile (strongly sorbed) forms of the electrolyte[17].

Another method of calculating diffusion coefficients is based on the Frisch equation[18], which in the case of concentration-independent diffusion coefficients reduces to the well known Dienes–Barrer equation

$$D_\theta = l^2/6\theta, \qquad (11)$$

where θ is the time-lag for the electrolyte–polymer system. In general, when D is a function of concentration, it can be expressed in terms of the directly measurable parameters θ and $\bar{P}$ (the permeability)[19]:

$$D_\theta = l^2\left[6\theta + 6\frac{d\theta}{d\bar{P}}\bar{P} + \frac{d^2\theta}{d\bar{P}^2}\bar{P}^2\right]^{-1}. \qquad (12)$$

At temperatures above the glass transition point of the polymer, and in the absence of interactions between the diffusing components, the diffusion parameters determined from the stationary and the non-stationary region of the kinetic curve are usually in good agreement over a wide range of concentration[20]. A variety of measuring cells can be used for the measurement of diffusion coefficients; the apparatus usually consists of two cells separated by the experimental polymer. The measuring cell contains a sensor which detects the arrival of electrolyte by diffusion through the polymer. Various methods of detection have been used: electrical conductivity[21,22], pH measurements[23–25], radioactive isotopes[26–29], chemical analysis[30–33], and optical methods[34]. Some of these methods give a direct measurement of the stationary concentration gradient of electrolyte in the polymer during diffusion. These include the layer removal method[35–37] and the multifilm method[38,39]. Knowing the concentration gradient and the flow of electrolyte we can calculate the diffusion coefficient, but in all these methods some uncertainty arises from the possibility of abnormal effects at the boundaries of the various layers.

Methods based on the measurement of permeability are fairly precise and convenient, but they suffer from the following complications. 1) Interactions between the flows of diffusing species. For example, it has been reported[40] that both the permeability and θ can vary during the counter-diffusion of water and electrolyte, and furthermore a new phase appears within the polymer. 2) Discrepancies between stationary and non-stationary diffusion coefficients. Usually $\bar{D} > D\theta$,[20] which may be due either to relaxation processes in the polymer occurring at a rate comparable to the rate of diffusion or to specific interactions such as water–oxygen interactions in hydrophobic polymers (see below). 3) The samples must be free from interconnected micropores and cracks, which would lead to erroneous results by allowing phase flow.

2. Methods Based on Measurements of the Properties of the Polymer–Electrolyte System

The measurement of diffusion parameters by these methods relies on directly or indirectly monitoring the amount of electrolyte in the polymer as a function of time. The equations describing the sorption kinetics for different initial and boundary conditions are discussed in Ref. 41, which also describes the effect of sample geometry on sorption.

To keep the boundary conditions constant during sorption the amount of diffusant in the solution should be much greater than the maximum sorption in the polymer[41]. The following methods can be used to determine the diffusion coefficients of electrolytes in polymers.

Gravimetric method. This method can be used when the sorption of the different components occurs at widely different rates. Concentration is monitored by the methods listed in the previous section. Complications may arise from interactions between solvent and electrolyte flows. The best results are obtained in studies of volatile electrolytes, whose concentration is determined by desorption into the gas phase in a stream of inert carrier gas[42].

Radioactive isotope methods. These methods are very convenient not only for measuring diffusion coefficients but also for measuring the self-diffusion of individual ions and of associated molecules of the electrolyte.

An interesting application is the measurement of diffusion parameters by isotope exchange reactions in the diffusion-limited regime. The course of the reaction (for example, H–D exchange) can also be monitored by i.r. spectroscopy[43].

Spectral methods. The concentration of diffusant in the polymer can be determined by modern spectral methods: optical[44], NMR[45,46], ESR (if the diffusant is paramagnetic[47,48]), and spin-echo[49].

Electrical conductivity method. Four types of conduction are possible in a polymer under the influence of an electric field: ionic, protonic, electronic, and induced. The first two types are the most important during the diffusion of electrolyte solutions.

A full analysis of the conduction processes requires a knowledge of the extent of dissociation of the electrolyte, its hydration, and its interaction with the polymer. The difficulty of obtaining this information is obvious, and therefore the relationship between diffusion coefficients and electrical conductivity is seldom unambiguous over a wide range of experimental conditions[50]. For example, a transition from the ionic to the electronic mechanism of charge transfer occurs as the water content of the polymer decreases[51]. Temperature has a marked effect on electrical conductivity[52].

In many polymers (especially in hydrogels) we can expect Kohlrausch's law of independent migration of ions to apply:

$$\chi = \sum_i z_i c_i u_i \qquad (13)$$

where χ is the specific conductance and μ_i is the mobility of the ions in an electric field. If Eqn. (13) applies the integral diffusion coefficient of the ion in the polymer ($\bar{D}_i$) can be calculated by the expression

$$R_e^{-1} = \frac{z_i^2 F^2}{RT} c_{pi}\left[\left(\frac{2l_N}{D_N} + \frac{l}{K_i D_i}\right)\right]^{-1}, \qquad (14)$$

where R_e is the electrical resistance of a sample of unit cross-sectional area and length l, c_{pi} is the concentration of the ion in solution, l_N is the thickness of the unstirred layer, and K_i is the distribution coefficient of the ion between the polymer and the solution[1]. If we can ignore the resistance of the Nernst layer Eqn. (14) simplifies to

$$R_e^{-1} = \frac{(z_i F)^2}{RT} \frac{c_{pi} D_i k_i}{l} . \qquad (15)$$

The electrical conductivity is a sensitive function of both the strength and the frequency of the applied electric field. As we increase the voltage the ionic transport process is increasingly limited by the unstirred layers at the surface (rather than by the bulk of the membrane), because the conductivity of the membrane increases sharply with field. At low a.c. frequencies the conductivity is determined by the diffusion-induced polarisation of the unstirred layers. At high frequencies the relationship between the diffusion parameters and the electrical conductivity becomes more complex, because under these conditions the ions do not move across the membrane but merely oscillate within a small region.

The methods of determining mobility from electrical conductivity data have recently been reviewed[1,53]. Correct results are obtained with dilute solutions of electrolytes in porous[54] and in charged polymers[55]. As the concentration of the electrolyte increases the concentration dependence of the conductivity becomes non-linear because of the following effects: the increased potential step at the polymer–solution interface, the increased electro-osmotic flow of the solvent, and the increased relaxation effect[56].

The electrical conductivity of polymer membranes is measured by applying electrodes, which can be classified[57] into three groups: electrodes not in contact with the membrane, platinum electrodes, and mercury electrodes. Mercury electrodes appear to be the best, whereas electrodes of the second group give low results and those of the first group give high results. The methods and circuits used in measuring electrical conductivity are described in Refs. 58 and 59.

Other methods used to measure diffusion parameters include micro-hardness methods[60] and the ion-selective electrode method[61], which has been applied to biological systems.

3. Methods Based on Monitoring the Moving Boundary of Electrolyte in the Polymer

A characteristic form of micro-motion has been observed during studies of diffusion in systems including a polymer and a low-molecular substance: the motion of a diffusion front into the bulk of the polymer. The mean diffusion velocity of the particles is related to the observed macroscopic motion of these particles by Eqn. (8). In practice the rate of displacement of the electrolyte is measured with respect to the surface of the polymer, and therefore Fick's equation is conveniently expressed in terms of the characteristic Hittorf system (see Chapter II) with $w_S = 0$. For a relatively low concentration of diffusant in the polymer the solution of the continuity equation for this system

$$c_i = c_0 \left(1 - \operatorname{erf}\left[\frac{x}{2(Dt)^{1/2}}\right]\right) \qquad (16)$$

applies to a semi-infinite solid bounded by a plane at $x = 0$ and having initial ($c = 0$ for $x > 0, t = 0$) and boundary conditions ($c = c_0$ for $x = 0$, $t > 0$). Assuming that $c/c_0 = \text{const}$, i.e. monitoring the motion of a fixed concentration $c = c_X$, we obtain

$$x = \lambda t^{1/2}; \qquad (17)$$

where x is the depth of permeation of a boundary of diffusant of constant concentration c_X in time t, and λ is the permeation coefficient. The depth of permeation of the diffusant in the polymer can be determined by a variety of methods: autoradiographic[62], optical[63], interferometric[64], or by acid–base indicators[65].

The latter method is the most widely used, but it is difficult to apply to the polymer–electrolyte system. Two types of result have been reported in the literature: 1) different indicators change colour at almost the same value of x (suggesting an anomalous distribution of diffusant in the polymer (steep front), or that the chosen indicators have similar pK values), and 2) the colour change of different indicators occurs at different values of x. From these results we can determine the true distribution of diffusant in the polymer only if the relationship of the pK values of the indicators in the polymer matrix to those in water has been established by independent experiments. The concentration gradient of the electrolyte is assumed to be not very steep, so that the colour changes of indicators with different pK in the polymer will occur in different regions of the c–x curve. Thus the observed depth of permeation should be a function of the type of indicator used.

In organic solvents the mechanism of the colour change of the indicator is seldom known, and the pK values have not been determined. Furthermore the transition from aqueous to non-aqueous or mixed solvents often causes inversion of the pK values. For example, the colour change of Methyl Red in water occurs at a higher pH than that of Bromophenol Blue, but in alcoholic solutions the opposite is true. Since acids and bases in polymers can be treated (to a first approximation) as mixed solutions, all the uncertainties associated with the use of indicators in non-aqueous and mixed solvents apply to our system. Therefore, with rare exceptions (e.g. gels) the method of acid–base indicators cannot be used to measure the concentration of an acid or a base in a polymer matrix. We can only conclude that the concentration of acid in the coloured part of the resin is greater than in the colourless part.

Because of the difficulty of measuring concentration in a polymer many workers confine themselves to determining the "depth of permeation" at some time τ, or they use the poorly substantiated expression

$$D = x^2/a\tau, \qquad (18)$$

where a is an arbitrary number.

We should stress that the use of this formula can lead to an incorrect treatment of the often reported concentration dependence of the diffusion coefficient. It is better to use Eqn. (17), and to express the variation of λ with concentration by Eqn. (16).

Mention must be made of a method of correctly determining diffusion coefficients from the velocity of a diffusant front of constant concentration without a knowledge of c_X and c_0 (see Ref. 50, p. 209).

The description of the diffusion process becomes even more complicated in the presence of interactions between the electrolyte and the solvent, or of relaxation processes leading to a rearrangement of the polymer structure. These effects will be considered below.

IV. HYDROPHILIC POLYMERS

Hydrophilic polymers include those in which water is easily soluble [poly(vinyl alcohol) PVA, cellulose, etc.) and those in which water has a moderate solubility (polyamides, some polyesters, etc.). The diffusion of electrolyte in ion-exchange polymers has been studied in great detail, and several monographs on this topic have recently been published[2,13,66]. It is not the purpose of this review to discuss specifically the processes which occur in ion-exchange polymers, but we shall nevertheless examine some of their basic features when the conclusions are equally applicable to non-ion-exchange polymers.

1. State of the Electrolyte in Polymers

Some attempts to measure pH in a resin phase have been based on doubtful assumptions. One estimate[67] was made from the colour change of an indicator sorbed by the resin, another[68] by measuring the degree of dissociation of amino-acids in an adsorbed state. The results show a large difference between the pH values in solution and in the polymer, but they cannot be used to evaluate the dissociation constants of the ionogenic groups.

Three methods of determining the dissociation constants of electrolytes in polymers by applying the law of mass action are known: the spectrophotometric method[69,70], the sorption method[71], and the conductimetric method[69].

Table 1. Dissociation constants of electrolytes in polymers containing 60–70 wt.% of water (pK_1 is quoted for ampholytes).

System	pK_{diss}	References
PVA – H_3PO_4	3.1	69
PVA – *m*-nitroaniline	2.6	69
Dowex-50 – *m*-nitroaniline	2.5	70
Sulphonated polystyrene – glycine	2.5	71
KU-2 × 4 – glycine	2.3	71
KU-2 – glutamic acid	2.2	71

Dissociation constants measured in various polymer–electrolyte systems are listed in Table 1. The pK values are close to the corresponding values for aqueous solutions. The small difference between the pK values in the resin and in solution is explained by selective absorption of one of the forms of the sorbed electrolyte. For example, in the case of aliphatic amino-acids the selectivity of the resin towards the univalent cation is small, and not very different from the selectivity towards the zwitter-ion: hence the pK of the acid in the polymer is practically the same as in water. The selectivity for bivalent cations is higher as a result of the electrostatic interaction with the charged groups of the resin, and the dissociation of the amino-acid is displaced towards the formation of the bivalent cation[71]. The equality of the pK_1 values of phosphoric acid in poly(vinyl alcohol) and in water can be explained either by the presence of micropores in the polymer, allowing access to the aqueous solution[72], or by the formation in the polymeric alcohol of structures having the same affinity towards the ions as the aqueous solution.

We note that in the PVA–H_2O–KCl system (in the same concentration range) the dielectric constant (which influences the dissociation of the electrolyte) is lower than in water by a factor of two, whereas the kinetic parameter (electrical conductivity) is an order of magnitude lower[73].

The dissociation of sulphuric acid in polycaproamide has been studied by an electrical conductivity method[74]. By making a number of assumptions the authors concluded that sulphuric acid can dissociate in the polymer containing as little as 6% of water. Only the first ionisation is significant, with $pK_1 = 2.5$.

The behaviour of ions is largely determined by their hydration. It has been shown[75] that the self-diffusion coefficients of the alkali metal cations in sulphonated polystyrenes increase in the sequence $Li < Na < K < Rb < Cs$, in qualitative agreement with the radii of the hydrated cations. The influence of hydration on the self-diffusion of ions in these polymers is confirmed by the relative values of the self-diffusion coefficients of multivalent ions ($Th^{4+} < In^{3+} < Ca^{2+} < Na^{+}$), since it is well known that the number of water molecules in the hydration shell of an ion increases with the valency of the ion.

On increasing the parameter which characterises the stability of the hydration shell of anions $(z_i/(r_i - 0.25)$, where r_i is the crystallographic radius of the ion) a proportionate decrease was observed in the ability of salts to diffuse into cellulose acetates ($NaNO_3 > NaCl > NaF > Na_2SO_4$), accompanied by a change in selectivity in the opposite sense[77].

2. Main Theories of the Diffusion of Electrolytes in Polymers

The following theories have been proposed to explain the diffusion of electrolytes in polymers.

The Mackie and Mears theory[78] ascribes the lower diffusion coefficients of electrolytes in hydrophilic polymers (as compared with aqueous solutions) to the increased diffusion path produced by the presence of the macromolecules. In the absence of interaction between the functional groups of the polymer and the ions this effect can be allowed for by introducing the factor $[(1 + \varphi_2)/(1 - \varphi_2)]^2$, where φ_2 is the volume fraction of the polymer.

The discrepancy between experimental and calculated diffusion coefficients necessitated the introduction of a correction for the difference in viscosity (as compared with aqueous electrolytes)[79]. However the validity of this correction is doubtful because of the ambiguity of the concept of viscosity in polymers[80].

The Yasuda theory[81–83] is a development of the free volume theory specifically aimed at hydrophilic polymers. It is assumed that the free volume of a swelled membrane is determined by the mole fraction of solvent (φ_1). The diffusion coefficient of the electrolyte in the membrane becomes

$$\lg D = \lg D_w - k\varphi_1^{-1}, \qquad (19)$$

where D_W is the diffusion coefficient of the electrolyte in water and k is a proportionality constant related to the volume taken up by the migrating electrolyte and to the free volume of the whole system. Fig. 1 shows a plot of the logarithm of the diffusion coefficient of sodium chloride in copolymers based on polyacrylamide with different amounts of hydroxyl groups against the mole fraction of water in the polymer. Eqn. (19) is not obeyed at low mole

fractions of water. Two important conclusions stem from this theory: 1) in the case of ions we expect a linear plot of $\lg D$ against $\lg D_w - q_i$, where q_i is equivalent to the cross-sectional area of the ion, and 2) the higher the water content of the membrane, the less marked is this relationship.

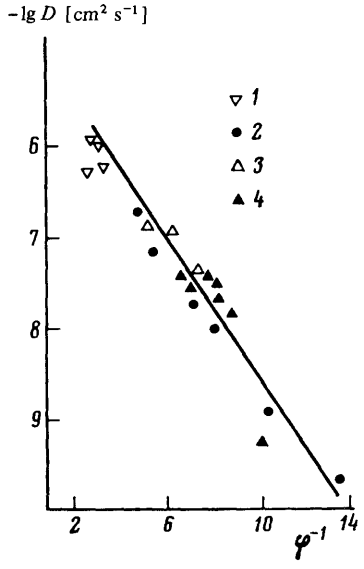


Figure 1. Diffusion coefficients in copolymers with different hydroxyl group contents against volume fraction of water in the polymer[81]: 1) hydroxyethyl methacrylate, 2) copolymers of methyl methacrylate with glyceryl methacrylate, 3) ditto with hydroxyethyl methacrylate, 4) ditto with hydroxypropyl methacrylate.

Boyd's approach[84] is a further development of previous theories. The decrease in mobility of ions upon being transferred from water into ion exchange polymers can be explained by three effects: a) the decrease in diffusion cross-section due to steric hindrance by the polymer network, b) the increase in the length of the diffusion path due to the need to avoid the polymer network, and c) interactions with pore walls. The relative importance of these three factors depends on the nature of the polymer and of the diffusant.

The model of Medley[85] and Marshall[86] is used to explain the dependence of the diffusion coefficients on the structure of polymers in which the solubility of water is limited. For example, in contrast to the case of high water solubility, the water dissolved in polyamides cannot form a continuous aqueous environment for the motion of the electrolyte in the polymer matrix. The water exists mainly near the polar end-groups, and to a lesser extent near the amide bonds. The ions diffuse by activated jumps from one polar group to another, passing through regions of low dielectric constant. For example, in polyhexamethylenediamine the distance between two nearest groups having the same charge is 30–40 Å, which probably determines the jump length.

If we assume that polyamides exist in a zwitter-ion form, the active centres for the diffusion of ions are the positively charged amino-groups, and those for the diffusion of protons the carboxyl groups.

Measurements of spin–spin and spin–lattice relaxation times for the polyamide–water system as a function of composition have shown that up to 0.5 wt.% of water can be present as water molecules strongly bound to the amide bonds. When the water content is increased from 0.5 to 8.0 wt.% the mobility of the water molecules in the polymer gradually increases to a level approaching the mobility of free water molecules. Addition of sodium chloride also increases the mobility of the water molecules: this effect is explained[87] by the ability of electrolytes to break down the clusters of H_2O molecules formed in the polymer.

3. Concentration Dependence of the Diffusion Coefficient

The most characteristic feature of the diffusion of electrolytes in hydrophilic polymers is the concentration dependence of the diffusion coefficients, which can arise in general from the following factors: a) a change in the degree of dissociation of the electrolyte, b) non-ideality of the thermodynamic behaviour of the polymer–electrolyte system, c) swelling of the polymer, causing increased mobility of the polymer segments, d) binding of the electrolyte by the ionogenic groups of the polymer.

We shall examine each of these factors separately. In practice factors b) and c) can be excluded by studying the diffusion of dilute solutions of electrolytes in polymers free from ionogenic groups and previously saturated with solvent.

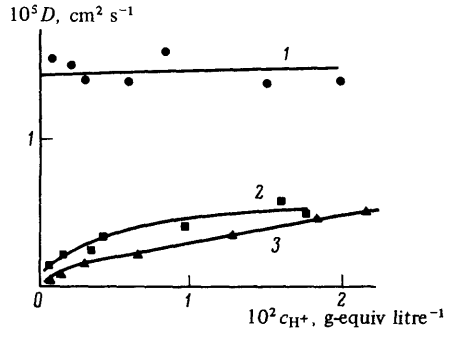


Figure 2. Concentration dependence of the diffusion coefficients of acids in PVA[25]: 1) HCl, 2) H_2SO_4, 3) H_3PO_4.

a) Concentration dependence of the diffusion coefficient due to changes in the degree of dissociation of the electrolyte

The effect of factors a) and b) stems directly from Eqn. (5). Fig. 2 shows the concentration dependence of the diffusion coefficients of acids in poly(vinyl alcohol) at 25°C. The diffusion coefficients were measured under steady-state conditions from the change in concentration of hydrogen ions in the measuring cell[25].

For a fully dissociated electrolyte (e.g. a dilute solution of HCl) Eqn. (5) can be simplified to

$$\bar{D}=D_{AC}\equiv D_{H^+(Cl^-)}, \qquad (20)$$

Solutions of H_2SO_4 of similar concentration show substantial dissociation up to the second ionisation, and hydrogen ions diffuse through the polymer matrix with the counterions HSO_4^- and SO_4^{2-}. Allowance for dissociation leads to the equation

$$\bar{D}=D_{H^+(HSO_4^-)}\left[1+2\left(\frac{f-2}{[c_{H^+}/K_2+2]^2}\right)\right], \qquad (21)$$

where c_{H^+} is the concentration of hydrogen ions, K_2 is the second dissociation constant of sulphuric acid, and $f=D_{H^+}(SO_4^{2-})/D_{H^+}(HSO_4^-)$. In the case of the weaker acid H_3PO_4 only the first ionisation is important in this range of concentrations:

$$\bar{D}=D_{H^+(H_2PO_4^-)}\left[1+\frac{2\beta}{K_1}c_{H^+}\right], \qquad (22)$$

where $\beta=D_{H_3PO_4}/D_{H^+}(H_2PO_4^-)$, and K_1 is the first ionisation constant of phosphoric acid.

During the diffusion of phosphoric acid in poly(vinyl alcohol) some of the diffusant molecules are bound in the polymer matrix and do not contribute to the mass transfer. In Eqn. (22) all the parameters relate to the free molecules of phosphoric acid.

The concentration of acid bound to the polymer is calculated by the Langmuir equation.

Table 2. Diffusion coefficients (10^6D, $cm^2\,s^{-1}$) of the ionised forms of acids in PVA and in water[25].

Ionised form of the acid	PVA	Aqueous solution
$H^+(Cl^-)$	14.4	30.0
$H^+(HSO_4^-)$	5.9	12.0
$H^+(SO_4^{2-})$	1.8	3.6
$H^+(H_2PO_4^-)$	1.2	16.1

The diffusion coefficients in PVA of HCl, H_2SO_4, and H_3PO_4 (a strong monobasic acid, a dibasic acid, and a partially dissociated acid) calculated by Eqns. (20) and (22) are given in Table 2. These values are quite close to the diffusion coefficients of the same acids in water. We may conclude that in a polymeric matrix containing 78 vol.% of water the presence of the polymer has little effect on diffusion, because the molecules and the tons of the acid are effectively screened by the water from interactions with the polymer. Hence the only obstacle to diffusion is the need to avoid the PVA macromolecules (except in the region of low concentrations). The theory of Mackie and Mears, which allows for this type of obstacle[78], yields diffusion coefficients close to the experimental values.

The self-diffusion coefficient of the hydrogen ion is approximately an order of magnitude greater than the self-diffusion coefficients of the anions and of the undissociated molecules in PVA.[69] This very high mobility of the proton is difficult to explain in terms of size only, particularly since the protons in the polymer matrix are in a hydrated state. The anomalously high value of $D^0_{H^+}$ is probably due to the specific mechanism of migration of the proton in a hydrophilic matrix, similar to the "relay" mechanism[88].

b) Concentration dependence of the diffusion coefficient due to thermodynamic non-ideality of the polymer–electrolyte system

In the previous section the diffusion of an acid was treated as the diffusion of an electrolyte showing practically ideal thermodynamic behaviour. However as the volume fraction of water decreases we must expect the polymeric molecules to influence the diffusion of the electrolyte, and the system to deviate from thermodynamic ideality. Thus, in the case of a polymer containing 38 vol.% of water the experimental diffusion coefficients of phosphoric acid are different from the values calculated by Eqn. (22). It is reasonable to assume that the difference is due to non-ideality of the diffusion system: in this case we obtain from Eqn. (5) the expression for the mean molar activity coefficient of the ions ($y_\pm$)

$$\lg y_\pm = 0.869\int_0^{c^{1/2}}\frac{D/D^0-1}{v}\,dv, \qquad (23)$$

where $v=c^{1/2}$. Graphical solution of this equation gives $y_\pm$. The results are discussed in Ref. 69.

c) Diffusion complicated by relaxation processes

In polymers close to and below the glass transition temperature the diffusion processes cannot be described in terms of Fick's equations with constant boundary conditions and with a diffusion coefficient depending only on concentration. Diffusion under these conditions is usually termed anomalous.

Anomalous diffusion is characterised by the following criteria[89]: a) the sorption plots of M_t/M_∞ against $t^{1/2}/l$ (where M_t and M_∞ are the amounts of electrolyte sorbed at time t and at equilibrium respectively) are not monotonic, but show characteristic points of inflection or are S-shaped; b) the kinetic sorption curves depend on the thickness of the sample; c) the plots of permeability against time can have maxima or minima in the non-stationary portion, and the time-lag does not obey the modified Frisch equation (12); d) the displacement of the moving boundary of the electrolyte solution is proportional to t^n (where $\frac{1}{2}<n\leqslant 1$) rather than to $t^{1/2}$ [as required by Eqn. (17)].

Several theories have been proposed to describe anomalous diffusion in polymers, but they can all be reduced to two: the molecular relaxation model and the diffusion–convection model[90].

The molecular relaxation model allows for the structural rearrangement of the macromolecules accompanying the penetration of the diffusing species into the polymer matrix[91,92]. At temperatures close to and below the glass transition temperature of the polymer the relaxation times of the molecular segments are similar to (or greater than) the characteristic times of the diffusion process. The case in which the rate of transport is limited only by the relaxation of the macromolecules is often called type II diffusion to distinguish it from diffusion according to Fick's law, which is termed type I diffusion. The criterion for type I diffusion is the applicability of Eqn. (17) to the motion of the diffusant boundary[93].

The effect of molecular relaxation is a time-change (by the first-order equation) in the concentration of diffusant in the surface layer [90,92] or in the diffusion coefficient [91]. For example, the change in surface concentration (c_t) with time is described by the equation

$$c_t = c_0 + (c_\infty - c_0)(1 - \exp[-t/\bar{\tau}]), \quad (24)$$

where c_0 is the surface concentration of diffusant at $t \to 0$, c_∞ is the equilibrium concentration of the diffusing species in the polymer, and $\bar{\tau}$ is a proportionality coefficient which characterises the mean relaxation time of the macromolecules [94,95].

Solution of Fick's equation with asymmetric boundary conditions [a surface concentration varying according to Eqn. (24)] for steady-state transport leads to the expression [96]

$$\frac{\theta}{l^2} = \frac{1}{6\bar{D}} + \bar{\tau}\left(1 - \frac{c_0}{c_\infty}\right) l^{-2}. \quad (25)$$

Eqn. (25) has the following properties: a) it explains the dependence of the diffusion coefficient $D\theta$ obtained from the non-stationary portion of the permeation curve upon the thickness of the sample; b) it explains the difference between diffusion coefficients determined under stationary and non-stationary conditions respectively; c) it shows that the time-lag experimentally observed in relaxing systems is equal to the sum of the time-lag associated with diffusion by Fick's law and of the time to reach the equilibrium concentration in the surface layer (characterised by the parameter $\bar{\tau}$).

Though the molecular relaxation model can explain a wide range of experimental results it relies on a number of empirical parameters whose physical significance is not always sufficiently clear. Therefore a full understanding of the effects involved in anomalous diffusion is impossible without additional information, obtained independently.

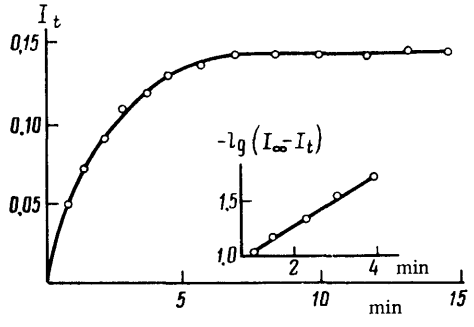


Figure 3. Time dependence of the intensity of absorption of an aqueous solution in PVA at 1675 cm^{-1}. Insert: graphical solution of Eqn. (24) [99].

The diffusion–convection model applies to strongly swelled glassy polymers. In the limit we observe the motion at constant speed of a sharp front separating the swelled outer layer from the unswelled inner layer [93,97]. In this case the motion of the liquid as a whole, under the influence of various forces, causes transport of the electrolyte dissolved in the liquid at a rate equal to that of the liquid. In some cases the motion of the front of diffusant can occur by an intermediate law,

$$x = \lambda t + \lambda t^{1/2}, \quad (26)$$

which is the sum of Fick's law diffusion and type II diffusion. The diffusion–convection model satisfactorily accounts for the experimental results except when the sorption curves are concave to the time axis [90].

The relaxation and the convection model described above can explain practically any anomalous diffusion phenomenon (except those associated with micro-cracking of the polymer [98]) and, in spite of some lack of physical clarity, they are the only means of describing and interpreting diffusion processes in glassy polymers.

In PVA below T_g we expect the relaxation processes to be slow, and to influence the surface concentration of diffusant. A change in the concentration of the aqueous solution in the surface layer of a PVA film (equivalent to 1% of the total thickness of the film) has been observed experimentally [99] by total internal reflection in the i.r. region. The choice of this thickness of surface layer was arbitrary, and determined primarily by the sensitivity of the measurement. Since a concentration gradient is produced in this layer, the calculation was based on an average concentration $\bar{c}_t$,

$$\bar{c}_t = \int_0^{l_m} c(x)\,dx/l_m,$$

where l_m is the effective depth of penetration of the light beam. The change of $\bar{c}_t$ with time was described by Eqn. (24). Fig. 3 shows the absorption intensity at 1675 cm^{-1} as a function of time for the surface layer of PVA, and a graphical solution of Eqn. (24). The $\bar{\tau}$ values are found to depend on the structure of the polymer.

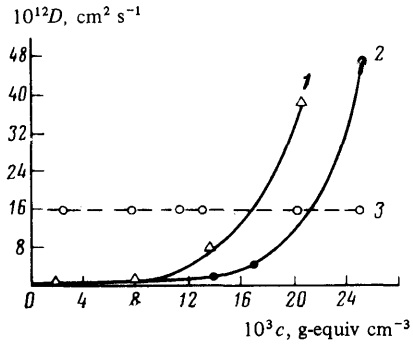


Figure 4. Concentration dependence of the diffusion coefficients in a polyamide [86] of: 1) HBr, 2) H^+, 3) Br^-.

d) Concentration dependence of the diffusion coefficient due to the presence of ionogenic groups in the polymer

The most detailed studies of the concentration dependence of diffusion coefficients relate to the sorption of acids by polyamides. Most workers report a large increase in diffusion coefficient with the concentration of electrolyte in solution [100–108] (see Fig. 4). These results

are explained by assuming that the electrolyte (acid) is sorbed successively by the amino groups and the amido groups of the polyamide, which exists in a zwitter-ion form. The causes of the observed increase in diffusion coefficient are the following.

1. The relative number of mobile ions in the polymer increases (as compared to the ions sorbed on the ionogenic groups).

2. The dielectric constant of the polymer increases with the concentration of the polar diffusant, leading to enhanced dissociation of the acid electrolyte and to generation of the more mobile ionic forms (protons).

3. The transfer of the acid from the amino to the amido sorption region shortens the distance between the positively charged groups of the polymer. This increases the probability of the "jump" of an anion from one positively charged group to the next through the non-polar medium provided by the weakly swelled polymer[86]. For example, keratin contains approximately 30 times more charged groups than Nylon-66, and as a result the self-diffusion coefficients in keratin are ~ 300 times greater than in Nylon. On the other hand uncharged molecules diffuse at comparable rates in these polymers, confirming the important role of electrostatic interactions in the polymer.

In the case of sulphuric acid the increase of the diffusion coefficient with concentration is due to the greater mobility of the hydrogen sulphate as compared with the sulphate ion[85]. It is assumed that the ratio of the first and the second dissociation constant of sulphuric acid is the same in the polymer as in the solution.

Table 3. Self-diffusion coefficients (D, $cm^2\ s^{-1}$) of ions and of alcohols in polyamides[85].

Diffusant	Polycaproamide	Poly(hexamethylene diamine)	Keratin
H^+ (free)	—	$3\cdot10^{-8}$	$8\cdot10^{-6}$
H^+ (bound)	—	$6\cdot10^{-13}$	$1.2\cdot10^{-10}$
Br^-	—	$6\cdot10^{-11}$	$2\cdot10^{-8}$
HSO_4^-	$1.1\cdot10^{-6}$	$6.8\cdot10^{-10}$	$2.2\cdot10^{-8}$
SO_4^{2-}	$1.9\cdot10^{-7}$	$2.0\cdot10^{-13}$	10^{-11}
CH_3OH	—	$1.0\cdot10^{-7}$	$1.0\cdot10^{-7}$
C_2H_5OH	—	$6\cdot10^{-8}$	$6\cdot10^{-8}$

The diffusion coefficients of the proton were calculated independently by the Nernst–Hartley equation[6], assuming that the mobility of the proton is determined by the concentration of free ions. The anomalously high mobility of the proton in the polymer (as compared with other ions, see Table 3) suggests a special transport mechanism, similar to the "relay" model[6].

4. Effect of Water on the Diffusion of Electrolytes

When considering the diffusion of aqueous solutions of electrolytes in polymers with a high affinity for water we must inquire into the extent to which the transport of the electrolyte is affected by the competing (or independent) transport of water, and also into any structural changes in the polymer under the influence of a solvent as specific as water.

Studies of the diffusion of pure water in polymers are discussed in a number of reviews[109–111], and the kinetics and mechanisms of the sorption and diffusion of water in polymers are examined in detail. We shall only be concerned with those features of the transport of water which influence the mechanism of diffusion of electrolytes in polymers.

In the absence of capillary flow we have to consider two types of water transport: a) the diffusion mechanism, in which the driving force is a concentration gradient, and b) the viscous flow of water, in which the driving force is a difference in hydrostatic pressure between the two sides of the membrane. The relationship between the hydraulic (G) and the diffusional ($\bar{P}$) permeability is given by the dimensionless coefficient w according to the equation[112]

$$w = GRT/\bar{P}\bar{V}_{H_2O}, \qquad (27)$$

where $\bar{V}_{H_2O}$ is the molar volume of water. The parameter w is unity for the diffusion mechanism, and increases as we move towards a viscous flow regime.[113]

We must identify the type of transport if we wish to interpret the kinetic results correctly and to arrive at valid conclusions on the interactions between the flows of water and of electrolyte in the polymer. In the diffusion mechanism this interaction is unlikely, but in the case of viscous flow of the solvent through a membrane we can expect interaction between the flows of the components of an aqueous solution of electrolyte[113]. Since most diffusion measurements are made without an excess hydrostatic pressure of solvent we can assume that diffusional transport is predominant (at least, in the case of moderately swelled polymers).

The absence of interaction between opposing flows of electrolyte and of water in a hydrophilic system (acetyl cellulose) has been demonstrated[114] by comparing the forward and the reverse osmosis of sodium chloride solutions.

When discussing the ingress of an aqueous solution of electrolyte into a polymer we must consider the water content of the polymer matrix, since the specific state of the electrolyte (i.e. its dissociation and its hydration) are determined by it. Furthermore active absorption of water weakens the intermolecular interactions, increasing the mobility of the polymer segments and hence increasing the diffusion coefficients.

Another factor which must be considered when discussing the diffusion behaviour of electrolytes is the state of the water in the polymer. Three types of system can be formed by the interaction of the polymer with water: a) the water dissolves in the polymer with formation of a uniform, quasi-homogeneous medium, b) local groupings (clusters) are formed[109,115–117]), and c) the interaction results in filling of the macro-structural holes, pores, and capillaries (which may be either interconnected or isolated)[118,119].

Recent work by electrical conductivity and NMR methods (among others) has shown that macromolecular gels contain both free and quasicrystalline water[120]. The transition temperature of the latter form is below 0°C. In addition to these two forms we must also consider an intermediate form with its own distinct electrophysical and thermal properties[121,122].

The great variety of possible structural forms of the solvent in polymers makes it difficult to identify the mechanism of ion transport.

5. The Moving Electrolyte Boundary

The diffusion of electrolytes in hydrophilic polymers may involve, as was stated above, on the one hand specific interactions between the components of the diffusing

medium and the polymer and on the other hand interactions between the components themselves in the polymer matrix. Depending on which of these effects is predominant the motion of the electrolyte solution can occur as a single front or as a macroscopic distribution of flows. Experiment shows that the former situation is more typical of polymers in which the solubility of water is limited.

Fig. 5 shows the change in concentration of water and HCl in a film of ethyl cellulose during the diffusion of hydrochloric acid vapour. The concentration of water was determined gravimetrically, and that of HCl by a chemical desorption method and by a combustion method [123].

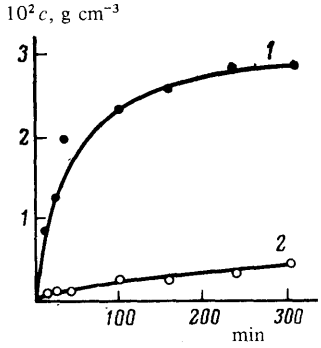


Figure 5. Kinetic curves for the sorption of H_2O (*1*) and HCl (*2*) in ethyl cellulose [123].

The diffusion of electrolyte solutions in polymers very often gives rise to a sharp boundary between a region containing the electrolyte and a region in which no electrolyte is detected by the analytical method employed. The reasons for the formation of this sharp boundary have been discussed [124-126], and the following explanations have been suggested: a) a chemical reaction between the components of the diffusion system, and b) a sharp change in the structure of the polymer at the boundary between the swelled and the free zone.

The interaction between an acid and water has been shown [19] to produce a boundary of constant concentration of electrolyte whose motion is described by Eqn. (17) with

$$\lambda = [2D(c_0/c_x - 1)]^{1/2},$$

if the electrolyte and the solvent are diffusing as a single front, and

$$\lambda = (\pi D)^{1/2}(1 - c_x/c_0),$$

if the electrolyte and the solvent are diffusing at different rates as separate flows. For example, the diffusion of an aqueous solution of sulphuric acid in polycaproamide is typical of case a). The calculated value $D = (1.5 \pm 0.2) \times 10^{-9}$ cm^2 s^{-1} is close to D_{H_2O} in polycaproamide. The time for contact between the two oppositely moving fronts in diffusion from both sides has been used [127] to calculate diffusion coefficients. The motion of the boundary in the polymer in its most general formulation is discussed in Ref. 128.

V. HYDROPHOBIC POLYMERS

One of the main characteristics of the transport of an electrolyte in hydrophobic polymers is the large difference in the rates of diffusion of different electrolytes. For example, the penetration of nitric acid through a Fluorlon-42 film 0.1 mm thick can be detected in 20–30 min, whereas over a year is needed with sulphuric acid [129]. In many cases the diffusion of electrolytes in these polymers is immeasurably slow.

We should note that permeability (as opposed to non-permeability) of a polymer by a particular electrolyte can usually be established with greater confidence. This is because the failure to observe permeation may be due to inadequate sensitivity of the method of detection or to insufficient time for diffusion. Evidently in this case it is better to characterise the permeability by the quantity $\bar{P}_{arb}$, calculated by the equation

$$\bar{P}_{arb} = c_{min} Vl/s\tau_0,$$

where c_{min} is the minimum concentration of electrolyte which can be detected by the chosen analytical method, and V is the extent of the medium in which transport is taking place through a film of thickness l and working surface s in time τ_0. If no penetration is detected we can only state that the true permeability of the system is less than $\bar{P}_{arb}$.

Table 4. Diffusion coefficients of electrolytes in hydrophobic polymers (c is the concentration of electrolyte in the aqueous solution).

Polymer	Electrolyte	c, wt.%	Temp., °C	D, cm^2 s^{-1}	Method of detection	References
Polyethylene	HNO_3	98	50	$2.9 \cdot 10^{-7}$	sorption	134
Polyethylene (NP)	HCl	28—36	50	$8 \cdot 10^{-7}$	sorption	135
Polyethylene (NP)	NaCl	1—10	20	$(6-8) \cdot 10^{-11}$	radio-isotope	136
Polyethylene (NP)	NaI	—	24	$2.2 \cdot 10^{-8}$	radio-isotope	137
Teflon-4	HNO_3	98	50	$2 \cdot 10^{-9}$	sorption	134
Teflon-4	NaI	—	24	$9.6 \cdot 10^{-9}$	radio-isotope	137
Teflon-4	NaCl	1—10	20	$2-3 \cdot 10^{-11}$	radio-isotope	136
Teflon-3	HNO_3	98	50	$7.7 \cdot 10^{-9}$	sorption	134
Teflon-3	NaI	—	24	$9.6 \cdot 10^{-9}$	radio-isotope	137
Polystyrene	NaI	—	24	$25 \cdot 10^{-8}$	radio-isotope	137

The permeability of polymers to electrolytes has been compared with the volatility of the electrolytes [130-132], with the conclusion that the permeability of hydrophobic polymers to involatile electrolytes is at least three orders of magnitude lower than their permeability to volatile electrolytes. The low diffusivity of involatile electrolytes is ascribed to negligible sorption of these electrolytes in polymers. This classification into volatile and involatile electrolytes is useful in qualitative predictions of the permeability of polymers towards specified electrolytes by using only generally available tabulations. After studying the transport of electrolytes in polyester resins Alt [133] classifies electrolytes as "strongly diffusing" (HCl, HF, HNO_3, H_2SO_4), "weakly diffusing", and "involatile". We must stress the arbitrariness of the distinction between "volatile" and "involatile" electrolytes. For example, the permeation of sulphuric acid through Fluorlon is easily detected at high temperatures and concentrations, when the vapour pressure of sulphuric acid is only a few thousandths of a mmHg.

Many measurements of the diffusion coefficient D in polymers have been reported, but in most cases the method used was inadequate[50]. Some results obtained by acceptable methods (see Chapter III) are listed in Table 4. We note the following facts. The diffusion coefficients of NaI in all the polymers examined are similar ($\sim 10^{-8}$ cm^2 s^{-1}), and almost three orders of magnitude higher than the diffusion coefficient of NaCl, although the molecular weight of NaI is almost twice that of NaCl. Obviously, the D value for sodium iodide is anomalously large: this may be due to reduction of the iodide ion to I_2.[138] The diffusion coefficients of HCl and HNO_3 in polyethylene are similar, and their relative values are consistent with expectations from the molecular weights of the two acids. They are of the same order of magnitude as the diffusion coefficient of benzene in polyethylene (at "zero" concentration) 1.32×10^{-7} cm^2 s^{-1}.[17] The diffusion coefficient of NaCl is several orders lower than the diffusion coefficients of HCl and HNO_3. No explanation of this fact has so far been offered.

1. Effect of the Concentration of Electrolyte in the External Solution on the Transport Parameters

The effect of the concentration of electrolyte in the external solution on the diffusion coefficients in the polymers presents a difficult problem. For example, in the polyethylene–HNO_3 system the D value decreases by a factor of 1.5 when the concentration of the acid is increased from 45 to 60%.[134] However these results are not very reliable, because they were obtained from kinetic data on the change in weight of samples immersed in aqueous solutions and they do not describe the diffusion of the acid itself. An analysis[139] of kinetic sorption curves gave very complex results. Evidently, the Johnston equation (which can be used to calculate D for a one-component diffusant) is not directly applicable to these systems.

The D value for nitric acid in polyethylene was found[140,141] to increase from 3.2×10^{-10} to 9×10^{-10} cm^{2}s^{-1} as the concentration of the acid in the external solution changed from 7 to 80%. It was determined by measuring (as a function of time) the electrical conductivity of a membrane in contact with the acid solution. These results are three orders of magnitude lower than the more reliable results reported in Refs. 134 and 142. The discrepancy probably arises from the failure to detect the diffusion of neutral particles in the electrical conductivity method.

The diffusion coefficients of HCl and H_2SO_4 in films of the KhSL lacquer (based on a perchlorovinyl resin) have been measured[27] as a function of concentration of the acid solution. At 60°C the coefficient D_{HCl} increases from 3×10^{-9} to 7.5×10^{-9} cm^2 s^{-1} as the acid concentration increases from 25 to 30%, and $D_{H_2SO_4}$ increases from 4×10^{-10} to 19×10^{-10} cm^2 s^{-1} as the concentration increases from 50 to 90%. The authors ascribe the concentration dependence of D to the transport of particles of different kind and different size from solutions of different concentration.

We have studied[135] the concentration dependence of D_{HCl} in polyethylene. The diffusion coefficients were determined by the method of Dienes and Barrer, and they were also calculated by the formulae

$$\bar{D} = \bar{P}[c\rho]^{-1}, \tag{28}$$

$$D = \frac{1}{\rho}\frac{d\bar{P}}{dc}, \tag{29}$$

where ρ is the density of the polymer and c is the concentration of HCl in the polymer. For comparison we also measured D for dry HCl at different partial pressures. We found that $\bar{D}$ increases with the concentration of the acid, approaching the value for dry HCl. The latter is independent of the partial pressure of HCl. The differential diffusion coefficient was found to be independent of the concentration of hydrochloric acid and equal to D for dry HCl. These observations were explained and quantitatively described by postulating the presence of "free" HCl and "hydrated" HCl in the polymer[135].

It was also assumed that the hydrated molecules are practically immobile and do not contribute to the transport process. The conclusion was that under steady-state conditions D_{HCl} does not depend on the concentration of hydrochloric acid. On the other hand under non-stationary conditions the effective diffusion coefficient varies because some of the diffusing molecules of acid are bound in hydrates, and therefore the integral diffusion coefficient $\bar{D}$ depends on the concentration of water in the polymer. The following equations for the concentration dependence were obtained:

$$\begin{gathered}\bar{D} = D_0\gamma, \\ \bar{D} = D_0(1 + MK\sigma^n_{H_2O}h^n_{H_2O})^{-1},\end{gathered} \tag{30}$$

$$D = D_0\left[1 + \frac{6n\,(Kc_{H_2O})^{n-1}}{[(n-1)+2][(n-1)+3]} + \frac{6\,(Kc_{H_2O})^n}{(n+2)(n+3)}\right]^{-1}, \tag{31}$$

where γ is the activity coefficient of HCl in the polymer, defined as the ratio of the concentration of "free" molecules to the total concentration of HCl in the polymer, D_0 is the diffusion coefficient of the free HCl molecules, c_{H_2O} is the concentration of "free" water molecules in the polymer, and the other symbols are defined above. From the $\bar{D}$ values determined by the method of Dienes and Barrer, together with Eqn. (31), we found the value of n (the number of H_2O molecules associated with one hydrated HCl molecule) to be 4.13 ± 1.69, which can be compared with the value obtained from sorption measurements[129–131] ($n = 5.01 \pm 1.28$). Thus consistent values of n were obtained in independent series of experiments, giving indirect confirmation of the validity of our postulate of hydrate formation. We should stress that these results were obtained for a single "polymer–acid" system, over a restricted range of HCl concentrations (28–34%), and at a single temperature (50°C), and therefore the problem of the dependence of the number of molecules in the hydrate upon the nature of the polymer and of the acid, the concentration of the acid, and temperature is still unsolved.

A rapid increase in the permeability of polymers with concentration of the electrolyte solution has been reported[130,143]. It is pointed out[131] that this rapid growth can be explained by assuming proportionality between the permeability and the vapour pressure of the electrolyte above its aqueous solution (which increases very rapidly with concentration). The concentration dependence of the permeability of films towards volatile electrolytes is accurately described by the expression

$$\bar{P} = \bar{P}_0 h, \tag{32}$$

where $\bar{P}_0$ is the permeability constant, independent of the concentration of electrolyte in the external solution, and h is the vapour pressure of the electrolyte over the aqueous solution[132,144]. Eqn. (32) was tested by studying the permeability of films to HCl, HF, and HNO_3.

2. Effect of the Nature of the Polymer on the Transport Parameters

Experimental data on the effect of the nature of the polymer on the diffusion coefficients of electrolytes are very few. We see from Table 4 that D_{HNO_3} in polyethylene is much greater than the diffusion coefficients in Fluorlons. This is consistent with the conclusion that gases have relatively low diffusion coefficients and relatively high solubilities in fluorine-containing polymers [145]. However in the case of the involatile electrolyte NaCl the diffusion coefficients in polyethylene and in Teflon are very similar. This may be due to differences in the diffusion mechanisms of HNO_3 and NaCl. Indirect information on the effect of the nature of the polymer on the diffusion coefficients of electrolytes in the polymer can be obtained from data on the permeation constants [Eqn. (17)].

The permeation coefficient is a function not only of the diffusion coefficient but also of the concentration of electrolyte solution in the surrounding medium. Sometimes it is also a function of the chosen method of detection [146]. Therefore it is important to ensure that when permeation coefficients are compared they are obtained under identical external conditions. The functional relationship between the permeation coefficient and the diffusion coefficient (and other factors) is not known in general. The following empirical relation applies to some systems [147]

$$\lambda_0 = A_0 h_a^b, \qquad (33)$$

where λ is the permeation coefficient, A_0 and b are empirical constants, and h_a is the vapour pressure of acid over the solution. For many polymer–electrolyte systems D can be evaluated from data on the concentration dependence of permeation coefficients [65].

The diffusion coefficients of NaOH, HCl, and H_2SO_4 in Pentaplast (3,3-bis(chloromethyl)oxacyclobutane polymer) have been measured [148]. At 40°C they are 1.4×10^{-5}, 0.4×10^{-5}, and 1.7×10^{-5} $cm^2\ s^{-1}$ respectively (radiometric method). These values are surprisingly high: thus, D_{HCl} in NP polyethylene, a material in which diffusion coefficients are relatively high, is only 8×10^{-7} $cm^2\ s^{-1}$. These high values of D are all the more remarkable in view of the low values of the permeability constant and of the permeation constant of HCl in Pentaplast in comparison with other polymers [149]. Equally surprising are the unusual dependences of the diffusion coefficients for volatile and for involatile electrolytes for water and nitric acid upon the logarithm of the permeation constants of these polymers for HCl. It follows that polymers can be classified according to their permeability towards electrolytes, as had been done previously for their permeability towards gases [150]. Fluorlon-3M has the lowest permeability of all the polymers examined. Within the Fluorlon series we note a clear correlation between the permeability for HCl and the permeabilities for HNO_3 and H_2O. The permeability for the latter diffusants is always much greater than that for HCl.

The introduction into hydrophobic polymers of polar substances or polar groups (carboxyl, carbonyl, or amino) invariably increases the permeability towards electrolytes, possibly as a result of increased sorption of the diffusant [142,151–153].

3. Effect of Temperature on Transport

The linearity of the plots of $\lg D$ against reciprocal temperature has been noted by many workers. The activation energies for diffusion E_D were calculated from these plots: some of the reported E_D values are listed in Table 5. Comparing these values with the activation energies for the diffusion of gases and vapours of similar molar volumes [17,50] we note that the former are somewhat lower. The cause of this phenomenon has not yet been analysed.

Table 5. Activation energy for the diffusion of electrolytes in polymers.

Polymer	Electrolyte	E_D, kcal mole^{-1}	Refs.
Poly(ethylene terephthalate)	H_2SO_4 (53%)	12	177
Poly(vinyl chloride) (plasticised)	HNO_3 (60%)	14	176
Poly(vinyl chloride)	HCl	3.3	176
Teflon-4	HNO_3 (98%)	4.5 (>323 K) 12.1 (<323 K)	134
Polycarbonate	HNO_3	10	178
Polyethylene	HNO_3 (98%)	4.3	179

Linear relationships are found also between the logarithm of the permeability constant λ and reciprocal temperature [147,154], but the physical significance of the "activation energies" calculated from these results has not been discussed.

The activation energy of the permeability has been determined [144] for HCl diffusing through polyethylene (PE), polystyrene, and poly(ethylene terephthalate): 8.5, 4.3, and 10 kcal mole^{-1} respectively. These values are typical of activated diffusion processes.

4. Views on the Transport Mechanism of Electrolytes in Hydrophobic Polymers

In the earlier work the permeation of electrolytes was treated as diffusion through interconnected pores (see, for example, Refs. 129, 155, and 156). However this model could not explain factors such as the high selectivity of the films, the concentration dependence of the permeability, and the high activation energies involved. A full analysis of the experimental information on the permeation of gases through polymer films has shown that in sufficiently thick films and at temperatures above T_g the mechanism of transport is diffusion rather than motion through a system of pores [157]. Therefore most workers now believe that the transport of electrolytes through hydrophobic polymers also occurs by diffusion.

These views on the mechanism of transport in hydrophobic polymers do not take account of the defects which may be present in a particular sample (for example, thin films may contain pores extending across the whole thickness of the sample, which are absent in thicker films of the same material). Transport associated with the presence of micro-defects has been discussed in some recent papers [158,159]. In particular, defects can be produced in polyethylene films by irradiation with a mercury lamp [160].

Various views have been expressed on the nature of the diffusing particles. According to some, the diffusing species are individual ions (hydrated, or not hydrated). According to others the diffusing species are undissociated molecules freed from their hydration shell. The resolution of this problem is complicated by the failure of some workers to distinguish between particles present in the polymer and particles responsible for matter transport.

The polymer must contain some particles able to transport matter, but there is no justification for the assumption that all particles present in the polymer can contribute to the transport process.

Let us consider the validity of the assumption that electrolytes are transported as ions in hydrophobic polymers. The concentration of ions in these polymers is probably low: this follows both from general considerations of the dissociation of electrolytes in media of low dielectric constant [161] and from experimental data. Films in contact with solutions of electrolytes keep a high electrical resistance [132,162]. In contrast, the electrical resistance of a hydrophilic film of PK-4 polyamide decreases by 7 orders of magnitude in 20–40 min after immersion in a solution of ammonium hydroxide [132]. Calculation shows [132] that if the whole of the HCl sorbed by polyethylene from hydrochloric acid solution were in an ionic form the electrical conductivity of the film would be 10 orders of magnitude higher than the experimental value. (See also Refs. 163 and 164 on the formation of ion pairs in polymers.) The fact that polyethylene films in contact with electrolyte solutions have a higher conductivity than films with metallic contacts has been ascribed to the adsorption of ions on the film surface [165,166].

The active conductance of plasticised poly(vinyl chloride) (PVC) is found [167] to be increased by diffusion of HCl: even involatile acids such as phosphoric acid diffuse readily in plasticised PVC [168,169], possibly as a result of the "hydrophilisation" of PVC by the plasticiser. The increase in electrical conductivity of hydrophobic polymers resulting from the addition of polar plasticisers has been discussed [170] in terms of the increased mobility and concentration of the ions in the polymer. Another possible explanation of the change in conductivity and dielectric constant of the films is chemical interaction between the diffusing species and the film, analogous to that observed in the "polyethylene–nitric acid" system [167].

It has been pointed out [170,171] that the activation energy for conduction is much higher than the activation energy for the migration of small molecules in polymers, the values for polypropylene and polystyrene being 34.6 and 30 kcal mole^{-1} respectively. These high activation energies for conduction are observed because they include contributions from the energy of the ionic "jump" (corresponding to the activation energy for molecular diffusion) and from the energy of formation of the ion (which is inversely proportional to the dielectric constant of the medium [172]). It has been suggested [170] that the ionic conductivity is determined mainly by ionisation under the influence of the electric field. In the presence of a sufficiently strong field the energy barrier is lowered and the conductivity increases as a result of the increased concentration of ions [173]. Thus the transport of electrolyte as ions in a hydrophobic polymer seems unlikely in the absence of an external electric field.

The hypothesis that transport occurs by undissociated molecules is supported by the following facts. The rate of transport of HCl through films of polyethylene, polystyrene, and poly(ethylene terephthalate), and of ammonia through polyethylene, does not depend on whether the electrolytes are diffusing from an aqueous solution or from the dry gas phase: in other words, the rate of transport under steady state is unaffected by the presence of water in the external phase [131,144]. Hence we conclude that the transport involves the same particles in both cases, and that these particles must be undissociated molecules free from their hydration shell since no other particles can be conceived in the case of diffusion from the dry gas. The lack of hydration shells around the diffusing molecules can be inferred also from the observed lack of dependence of the rate of transport of water from acid solution upon the nature of the acid. If the electrolyte were transported by hydrated particles we would expect the transport to be accompanied by varying amounts of water as a result of differences in the degree of hydration of different ions and of differences in the various flows. However it is found that for a given polymer the rate of transport of water is uniquely determined by the partial pressure of water vapour above the solution of acid [132,174].

In general [132,144] the transport of volatile electrolytes through films of hydrophobic polymers involves three steps: extraction of the electrolyte by the surface layer of the polymer, diffusion through the thickness of the polymer, and re-extraction on the far side of the film. Under steady-state conditions this process is analogous to the transport of gases, and is described by the equation

$$J = D(a_{1n} - a_{2n})/l \simeq Da_{1n}/l, \tag{34}$$

where J is the flow through a film of thickness l, D is the differential diffusion coefficient, and a_{1n} and a_{2n} are the activities of the electrolyte in the polymer on the near and the far side of the film respectively. The quantity a_{1n} is related to the activity of the electrolyte in the external solution (a_B) by the expression

$$a_{1n} = Ka_B, \tag{35}$$

where K is the thermodynamic distribution constant of the electrolyte between the polymer phase and the aqueous solution. Combining Eqns. (34) and (35) we obtain an equation for the permeability of the film as a function of the composition of the external solution, and of the properties of the diffusant and of the polymer:

$$J = DKa_B/l. \tag{36}$$

The product DK is, effectively, the permeability constant P_0, which depends on the properties of the polymer and of the diffusant, and the effect of the composition of the external medium on the permeability is uniquely determined by the quantity a_B. The parameter K is related to the standard change in free energy of extraction (ΔG°_e) by the equation

$$\Delta G^\circ_e = -RT \ln K. \tag{37}$$

The transfer of the electrolyte from the aqueous solution into the polymer can be described as the removal of the electrolyte from the aqueous solution (i.e. the reverse of dissolution) followed by the mixing of the electrolyte with the polymer:

$$\Delta G^\circ_e = -\Delta G^\circ_{sol} + \Delta G^\circ_m, \tag{38}$$

where ΔG°_{sol} is the standard change in free energy accompanying the formation of an aqueous solution at infinite dilution, and ΔG°_m is the standard free energy change on mixing the electrolyte and the polymer. Tentative calculations for acids have shown [132] that the main contribution to ΔG_e comes from the term $(-\Delta G^\circ_{sol})$, i.e. the energy needed to remove the electrolyte from the aqueous solution is determined mainly by the distribution constant. However differences in extractability are themselves related to differences in the ΔG°_m value, which is directly related to the amount of sorption by the expression

$$\Delta G^\circ_m = -RT \ln \varphi_1. \tag{39}$$

The quantity φ_1, i.e. the volume fraction of solute, can be calculated to a first approximation by using the Flory equation [175] in the simplified form

$$-\ln\varphi_1 = 1 + \bar{V}_1(\delta_1 - \delta_2)^2/RT, \qquad (40)$$

where $\bar{V}_1$ and δ_1 are the molar volume of the solute and its solubility parameter respectively, and δ_2 is the solubility parameter of the polymer. There is indirect evidence (weak concentration dependence of the permeability, similarity of the diffusion coefficients in different polymers) that Eqn. (36) does not apply in real systems.

The nature of the polymer, its affinity towards water molecules, and the concentration of water (which affects the physicochemical properties of the polymer) have a strong influence on the type and on the mechanism of the transport of electrolytes in polymer systems.

The diffusion of electrolyte solutions in hydrophilic polymers, in which the solubility of water is high, is characterised by equilibrium parameters (such as the dissociation constant and the diffusion parameters D, λ_0, and u_i) close to the values of the same parameters for solutions. The decrease in mobility of molecules and ions in a polymer (as compared to their mobility in solution) is due to the increased length of the diffusion path and to interactions between the diffusing particles and the polymer. In hydrophilic polymers with a limited water solubility the dissolved water cannot form a continuous aqueous environment within the polymer matrix, and the diffusion of ions occurs by activated jumps between polar groups, resulting in a D value much lower than in the solution.

The diffusion of electrolytes in hydrophobic polymers is similar (in general) to the diffusion of gases and vapours which are inert towards the polymer, but the interaction of water with the polymer has a substantial effect on the diffusion process during the initial non-stationary period.

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Non-isothermal Processes and Methods of Investigation in the Chemistry and Mechanics of Polymers

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We shall discuss kinetic processes relevant to the chemistry and the mechanics of polymers in which the internal evolution of heat (due to exothermic reactions or to dissipative deformation) exceeds the ability of the system to transfer heat to its surroundings, so that the chemical reaction or the mechanical process occurs under non-isothermal conditions at a rate which is dependent on temperature. Processes of this type include: non-isothermal polymerisation (in a batch or a flow reactor), thermal phenomena during the cyclic deformation, extension, and external friction of polymers, and flow under conditions of dissipative heating. We shall describe the common features of all these phenomena, their characteristics, and their most important consequences from the standpoint of research and technology. 164 references.

CONTENTS

I. Introduction 798
II. General theory of non-isothermal processes 798
III. Non-isothermal polymerisation 800
IV. Non-isothermal deformation of solid polymers 803
V. Non-isothermal flow 806
VI. Conclusions 808

I. INTRODUCTION

Many processes in the chemistry and mechanics of polymers are accompanied by evolution of heat. The resulting increase in temperature can affect the process very substantially if the relevant rate constants are strongly temperature dependent. Non-isothermal effects have many interesting and important consequences, and their study is an unusual and very revealing (though indirect) method of highlighting the basic features of the phenomenon under study.

The aim of this review is to discuss the non-isothermal processes of relevance to the chemistry and mechanics of polymers. The direct analogy which exists between these two topics justifies a common approach. Thus the analogue of the evolution of heat during polymerisation is the dissipative nature of deformation processes in all polymers. The analogue of the increased rate of a chemical reaction at elevated temperatures is the increased rate of the relaxation processes. In both cases the temperature rise is opposed by the transfer of heat to the surroundings, but the finite thermal conductivity of the reaction medium or of the polymer undergoing deformation gives rise to non-isothermal conditions. These analogies are by no means trivial, because the phenomena being compared are different in nature, and each phenomenon has its own specific features (such as the gradual disappearance of the monomer during chemical reaction and the formation of a new phase during polymerisation, or the relaxation into different physical states during deformation). Heat evolution during deformation is a well-known phenomenon for polymers in any physical (relaxation) state, and is due to internal friction or to the visco-elastic properties of most polymeric materials[1-4].

Thus the basic feature common to the whole of our discussion will be the dissipative nature of the polymerisation and mechanical deformation processes, which gives rise to an increase in the temperature of the reacting mass (deformation) and hence to an increase in the rate of the chemical reaction (relaxation).

II. GENERAL THEORY OF NON-ISOTHERMAL PROCESSES

The development of the theory of non-isothermal processes is closely associated with the theory of combustion. The work on combustion by Semenov, Zel'dovich, Frank-Kamenetskii, and others[5-7] laid the foundations of our understanding of chemical reactions under non-isothermal conditions. More recently the theory of non-isothermal processes has been further developed in connection with various problems in chemical technology[8,9] and in thermal analysis[10-12].

Non-isothermal processes can be classified in different ways, but the most rational classification relies on the origin of the non-isothermal behaviour. From this point of view we can distinguish two important classes of non-isothermal phenomena: internally non-isothermal and externally non-isothermal. Processes of the first class are characterised by constant external conditions, for example an invariant temperature at the surface of the reacting system. Non-isothermicity is produced by an internal source of heat, such as an exothermic or endothermic reaction, energy dissipation by viscous flow, etc. The power output of the source is usually strongly temperature-dependent, and therefore we can expect positive or negative feedback loops. Processes of this type are considered in detail in the theory of combustion.

The second class of phenomena includes processes with weak heat evolution. In this case the non-isothermicity arises mainly from changes in external conditions. Non-isothermal processes preceding the establishment of thermal equilibrium under constant external conditions are sometimes of interest. In both cases the thermal field in the system is not substantially affected by the internal source of heat, and the feedback is not marked. This situation often arises in the thermal analysis of reacting systems, and occasionally in chemical technology[9].

Exothermic processes of the first class are the most interesting. Their strong positive feedback produces specific non-isothermal phenomena which can only be

explained by combined heat evolution and heat transfer effects. These processes include thermal explosions, ignition phenomena, and the propagation of a thermal wave.

1. Thermal Explosion[13-16]

Consider a system including a source of heat with a high and strongly temperature dependent energy output (for example, an exothermic reaction with a large exoergicity and a high activation energy). The heat evolved by the reaction is partly transferred to the surroundings and partly retained in the system, leading to self-heating. The resulting temperature rise accelerates the evolution of heat by a positive feedback mechanism. Under suitable conditions the process can become self-accelerating and produce a thermal explosion if some well-defined critical (or limiting) conditions are met. Below the thermal explosion limit the exothermic reaction proceeds "quietly", with a small amount of self-heating in a stationary (or quasi-stationary) regime. Feedback effects are not very marked in this case.

The simplest form of the thermal explosion equations for condensed systems is

$$C\rho\frac{\partial T}{\partial t}=\lambda\left(\frac{\partial^2 T}{\partial x^2}+\frac{n}{x}\frac{\partial T}{\partial x}\right)+Q\rho k_0 e^{-E/RT}\varphi(\eta), \quad (1)$$

$$\frac{\partial\eta}{\partial t}=k_0 e^{-E/RT}\varphi(\eta), \quad (2)$$

$$\left.\begin{array}{ll} t=0 & T=T_0,\ \eta=0; \\ x=0 & \partial T/\partial x=0;\ \ x=r:\ -\lambda\partial T/\partial x=\alpha(T-T_0)\end{array}\right\}, \quad (3)$$

In these equations T is the temperature of the system, T_0 is the temperature of the surroundings, x is the spatial coordinate, r is the characteristic dimension of the reactor, η is the extent of conversion of the reactant, t is time, C, ρ, and λ are the specific heat, density, and thermal conductivity of the system, Q is the thermal effect (exoergicity) of the reaction (per unit volume), k_0 is the pre-exponential factor, E is the activation energy, α is the thermal emission coefficient, n is a geometric coefficient ($n = 0$ for a plane-parallel plate, $n = 1$ for an infinite cylinder, $n = 2$ for a sphere), and $\varphi(\eta)$ is the kinetic function. The problem consists in defining the critical phenomena: the critical condition (i.e. the relationship between the parameters which distinguish the two regimes, $F(T_0, r, \alpha\ldots) = 0$), and the induction period (the duration of the period of gradual temperature rise preceding the explosion, $t_{ind} = t_{ind}(T_0, r, \alpha\ldots)$).

The structure of the thermal field plays a very important role in the theory of non-isothermal processes. Both the amount of self-heating and the temperature gradients are usually small in the non-explosive regimes. Often Eqn. (1) is replaced by the simpler heat balance equation, ignoring spatial non-isothermality:

$$C\rho\frac{dT}{dt}=Q\rho k_0 e^{-E/RT}\varphi(\eta)-\alpha\frac{S}{V}(T-T_0), \quad (4)$$

where S is the heat transfer surface and V is the reaction volume. Eqn. (4) is physically justified when the Biot number is small ($Bi = \alpha r/\lambda \ll 1$),[17-19] and also under conditions of forced or free convective mixing[20,21]. A more general treatment of Eqn. (4) can be developed by introducing two new parameters: the average temperature and the effective heat transfer coefficient. The error introduced by using Eqn. (4) in general is small, because the temperature rise preceding the explosion is usually small.

2. Ignition[22,23]

During a thermal explosion the self-accelerating reaction occurs throughout the volume of the system, whereas during ignition it is localised (usually on the surface layer, under the influence of a powerful flow of heat from an external source). The mechanism and the rate of supply of heat are always important in ignition processes, and also the non-stationary thermal field in the system. The kinetic features of the source of heat are less important, because ignition occurs in the initial stages of the process. Ignition is often described by a single equation based on the model of a zero-order reaction:

$$C\rho\partial T/\partial t=Q\rho k_0 e^{-E/RT}+\lambda\partial^2 T/\partial x^2,$$

$t=0$ $\quad T=T_{init}$;

$x=0$ 1) $T=T_0$ (heated plate),

2) $-\lambda\partial T/\partial x=q_0$ (radiant flux of intensity q_0),

3) $-\lambda\partial T/\partial x=\alpha(T-T_0)$ (convective flow),

where T_{init} is the initial temperature.

We are sometimes interested in pulsed regimes, when the external source of heat acts for a limited time only. The commonest problems in ignition theory are to calculate the delay time of the ignition and the critical conditions (as in the case of the thermal explosion).

3. Propagation of a Thermal Wave[24-28]

This is the most interesting of the phenomena considered in the theory of non-isothermal processes. It is well known that a thermal wave cannot exist in an inert system: any injected heat pulse immediately decays. However, in systems including a non-linear source of heat which is strongly temperature dependent non-isothermal processes can become self-propagating, giving rise to a wave of temperature rise moving at constant speed through the "cold" substrate.

Thermal waves are described by the system of equations

$$C\rho\partial T/\partial t=Q\rho k_0 e^{-E/RT}\varphi(\eta)+\lambda\partial^2 T/\partial x^2, \quad (5)$$

$$\partial\eta/\partial t=k_0 e^{-E/RT}\varphi(\eta), \quad (6)$$

$$\left.\begin{array}{ll} t=0 & T=T_{init},\ \ \eta=0; \\ x=0 & T=T_{ign}>T_{init}, x=\infty,\ \partial T/\partial x=0\end{array}\right\} \quad (7)$$

and the solution is expressed in the form

$$T=T(x-ut),\ \eta=\eta(x-ut); \quad (8)$$

where u is the velocity of propagation of the wave and T_{ign} is the ignition temperature.

The sytem (5)–(7) also describes the ignition process which precedes the stationary propagation of the wave. The velocity of the wave is often determined from steady-state equations in a coordinate system for which the wave front is stationary and the reactants are moving towards the front:

$$\lambda\frac{d^2T}{dx^2}-C\rho u\frac{dT}{dx}+Q\rho k_0 e^{-E/RT}\varphi(\eta)=0, \quad (9)$$

$$u\frac{d\eta}{dx}=k_0 e^{-E/RT}\varphi(\eta), \quad (10)$$

$$\left.\begin{array}{ll} x=-\infty & T=T_0, \quad\ \eta=0, \ dT/dx=0, \\ x=+\infty & T=T_0+Q/C\rho, \ \eta=1, \ dT/dx=0.\end{array}\right\}. \quad (11)$$

The existence of thermal waves and their velocity usually depend on the total emission of energy from the heat source: in other words regimes with $\varphi(1) = 0$ are usually considered.

All these phenomena are critical, and they occur only if

$$\beta = \frac{RT_*}{E} \ll 1, \quad \gamma = \frac{C\rho}{Q} \cdot \frac{RT_*^2}{E} \ll 1, \tag{12}$$

where T_* is a scaling temperature which characterises the process. They are studied in the theory of combustion—the most important topic in the theory of non-isothermal processes. If the inequalities (12) are not extreme the phenomena tend to degenerate, and their boundaries become more diffuse.

In the case of endothermic processes the feedback loop is negative, and this simplifies the problem and leads to stable stationary regimes with varying degrees of non-isothermality.

Externally non-isothermal processes are very interesting in chemical kinetics because they offer the possibility of non-isothermal methods of investigation[10-12]. The course of a chemical reaction in these systems is almost entirely determined by the external conditions and by heat transfer, and the reciprocal effect of the reaction on the heat transfer process is unimportant. Under heat exchange conditions such that the temperature gradients in the reacting volume are small, and the system is able to "absorb" the small temperature changes produced by the heat of reaction, we can calculate the reaction rates and their dependence on temperature and on the extent of reaction, i.e. we can study the chemical kinetics of the system. This is usually done by imposing a linear temperature rise on the surrounding medium.

Non-isothermal processes are widespread in chemistry, physics, energetics, chemical industry, and other branches of science and technology. They are typical of oxidation reactions, thermal decomposition, synthesis from the elements, polymerisation, etc. Many physical processes such as nuclear reactions, phase transitions, viscous flow, the interaction of matter with high-frequency electromagnetic fields, etc. also occur in a non-isothermal regime[29]. The theory of non-isothermal processes and the ideas which have been developed from it are independent of the specific nature of the processes considered, and are based on the general phenomenological laws of heat evolution and heat transfer. Not surprisingly, therefore, we can legitimately rely on analogies and transfer results from one system to another when discussing specific non-isothermal processes.

III. NON-ISOTHERMAL POLYMERISATION

1. General Description

Polymerisation usually occurs under conditions of self-heating, produced by the exothermicity of the chain growth reaction. If the thermal effect of this reaction is small, the reaction rate is only weakly temperature dependent, and the viscosity of the reacting mass in the initial stages of polymerisation is low, then we can maintain approximately isothermal conditions and keep the temperature constant by vigorous stirring and by thermostatting the walls of the apparatus. On the other hand the temperature of the system will tend to increase continuously during polymerisation if the viscosity is high, the thermal conductivity of the mixture is low, and the thermal acceleration resulting from the temperature dependence of the reaction rate is large. Under the latter set of conditions polymerisation processes must be classified as non-isothermal.

Heat evolution effects have recently been recognised as a favourable feature in polymerisation reactions, often responsible for the practical success of a proposed reaction. Typical examples are adiabatic and frontal[30,31] polymerisation reactions, thermal initiation[32], etc. These methods allow us to impose "extreme" conditions on the reaction and thus to accelerate the polymerisation process.

The study of non-isothermal polymerisation is concerned with two basic problems. The first (or direct) problem consists in obtaining information on the process itself from data on the properties of the mass undergoing polymerisation (physical, rheological, and chemical). A macro-kinetic approach is used, and a model of the process is developed from the transport equations, the equations of chemical kinetics, and the equations of state. By solving this problem we arrive at the temperature distribution, the extent of reaction, and the structural characteristics (molecular weight distribution) of the product in space and in time.

The second (or inverse) problem consists in obtaining the characteristics of the chemical reaction (rate constants and activation energies) from information on the process itself, for example from the experimentally determined time dependence of the heat evolution or of the temperature at one point or at a small number of points. The solution of this problem usually involves the use of macro-kinetic relationships previously obtained by solving the direct problem.

Polymerisation processes can also be classified in terms of the complexity of the chemical reaction involved. The kinetically simplest polymerisation processes are those strongly dominated by a single reaction. A number of polycondensation and vulcanisation reactions[33,34] are of this type. Radical polymerisation reactions involve a more complex kinetic scheme which must, in general, allow for the initiation, growth, and breaking of chains[35].

We shall discuss the results of studies of the thermal regimes of polycondensation and radical polymerisation processes in chemical reactors of simple design. Some results on the macro-kinetics of ionic polymerisation are examined in Refs. 36 and 37, and will not be considered here. There are no published data on the macro-kinetics of emulsion, suspension, and other types of polymerisation under non-isothermal conditions.

2. Simple Kinetic Scheme

The thermal regimes of reactions of this type are generally similar to those of true or degenerate thermal explosion reactions. We can therefore describe the macro-kinetics of these polymerisation processes by applying the methods of the classical theory of thermal explosions (see above) in a static reactor. However due allowance must be made for some specific features of polymerisation processes, such as the lower values and the greater range of the heats of reaction (Q) and of the activation energies (E) of polymerisation processes as compared with explosive systems.

Temperature and concentration gradients cannot exist in an ideally stirred reactor. This model is described by the heat balance equation (4) and the kinetic equation (2). The system of equations (2)–(4) has been analysed[38,39] with special reference to polymerisation processes involving a wide range of the parameters Q and E. It was

found that three characteristic regions of thermal regimes are possible.

1) A region of non-degenerate thermal self-acceleration. Depending on the relative magnitude of the heat evolution and of the heat extraction, described by the Semenov criterion $\kappa = QE\rho k_0 \exp(-E/RT_0)/[\alpha(S/V)\cdot RT_0^2]$, the self-heating during polymerisation can be small (if $\kappa < \kappa_{cr}$) or large and rapidly increasing (if $\kappa > \kappa_{cr}$). The critical value κ_{cr} is very sharply defined. The extent of reaction during the development of the maximum heating rate is negligible, and therefore regimes corresponding to $\kappa > \kappa_{cr}$ are undesirable in polymer technology.

2) A region of degenerate thermal self-acceleration. In this case we have a sub-critical regime in which the rate of growth of the temperature is decreasing continuously, and a super-critical regime corresponding to thermal self-acceleration. However the transition between these two regimes is gradual (degeneracy of the critical conditions). The degree to which the polymerisation can be accelerated is limited by the availability of the monomer, and the extent of reaction during the development of the maximum temperature is considerable.

3) A region of thermal regimes without self-acceleration. In this region the rate of self-heating decreases with time, and the monomer has almost completely disappeared when the maximum temperature is reached.

The boundaries between these three regions are not sharp: they are determined by the values of the two dimensionless parameters $\gamma = C\rho RT_*^2/(QE)$ and $\beta = RT_*/E$, which describe the thermal effect and the activation energy of the reaction. The last two regions are technologically important.

Three thermal regimes exist also in the case of polymerisation in a batch reactor without stirring[40-42], to which the heat balance equation for conductive heat transfer (1) applies. Different boundary conditions for the temperature are possible. The heat dissipation conditions are usually defined in terms of the Biot criterion. Since the thermal field is not uniform over the cross-section of the reactor the extent of reaction is also, in general, not uniform. The degree of non-uniformity increases with the Frank-Kamenetskii criterion $\delta = Qk_0Er^2/(\lambda RT_0^2 e^{E/RT_0})$, which characterises the ratio of the rates of heat evolution and heat relaxation by conductive heat transfer. At low values of δ the polymerisation occurs fairly uniformly over the volume of the reactor (volume polymerisation). At large values of δ the reaction goes to completion first in the outer layers of the reaction volume, after which the polymerisation front moves towards the centre of the reactor (frontal polymerisation)[40,41].

The quantity η is the only kinetic characteristic in the initial equations (1), (2), and (4) on which the present discussion is based. This characteristic could be, for example, the concentration of monomer in the reaction mixture. However the structure and the properties of the product depend on a whole range of reactions of the growing chain, which yield polymers with different molecular weight distributions (MWD) and, in general, different amounts of chain branching. In non-isothermal polymerisation (which includes the vast majority of technological processes) the rate constants of the various steps of the polymerisation reaction have different temperature coefficients, and as a result the MWD can be very different from the distribution expected for isothermal polymerisation. This is a serious problem, which can radically alter the properties of the product (see, for example, Refs. 43 and 44).

A quantitative estimate of the effect of non-isothermicity on the MWD of the resulting polymer cannot be made in general, because the solution of the problem is sensitively dependent on the special kinetic features of the process. However we can develop a general approach to this problem by introducing the "generalised" time τ, defined by the pattern of the previous temperature changes. Thus in the case of anionic polymerisation with very fast initiation, when only the rate constant for chain growth (K) is relevant to the overall kinetics, the generalised time τ is given by[45]

$$\tau = \int_0^t K[T(t)]\, M(t)\, \mathrm{d}t, \qquad (13)$$

where M is the concentration of monomer in the reaction mixture (depending on time t), and K depends on temperature (which also varies with time). This approach allows us to calculate the MWD of the resulting polymer by postulating quasi-isothermal conditions with respect to the variable τ. Some technological aspects of the effect of non-isothermal polymerisation on the MWD of the resulting polymer are discussed in Refs. 46 and 47.

We must stress that a very similar approach, relying on the use of a "generalised" time, had been developed previously[48] to describe non-stationary processes during visco-elastic relaxation. The approach can be applied to any non-isothermal deformation or relaxation phenomenon, making the system quasi-isothermal. The most detailed studies in this area have been on problems of polymer creep[49,50].

3. Radical Polymerisation

The macro-kinetics of radical polymerisation under non-isothermal conditions were first investigated by Maksimov[31,51-53], who combined the kinetic equations for chain growth and initiator decomposition with the heat balance equation (1) on the assumption of constant concentration of free radicals during the polymerisation (quasi-stationary hypothesis).

Because of the kinetic peculiarities of radical polymerisation, new and interesting types of behaviour are possible. The basic kinetic feature, associated with the consumption of the initiator, is that high levels of self-heating are not reached in the "explosion" regime (because of the rapid "burning up" of the initiator). Another characteristic feature of radical polymerisation is the gel effect, which consists in an increased rate of polymerisation as a result of the increase in viscosity (and decrease in the rate of chain breaking) as the extent of reaction increases. Corrections for the gel effect in macroscopic treatments are usually applied by various empirical formulae[53-55]. Under non-isothermal conditions the increase in temperature assists the motion of macrochains, and the gel effect is displaced towards higher extents of reaction (or is eliminated).

The gel effect during radical polymerisation produces a new thermal regime, called the intermediate regime[53]. In this regime the self-heating is small during the initial stages of polymerisation, but in the later stages the reaction rate increases rapidly and the mixture reaches high temperatures.

4. Propagation of the Polymerisation Front

The polymerisation reaction can occur in layers, with a propagating polymerisation front, the heat evolved in the reaction zone being taken away by the colder layers in which the reaction had started. This "frontal" polymerisation regime has considerable practical importance because it offers lower working temperature and lower polymerisation (shrinkage) stresses.

Enikolopyan and coworkers[56-59] describe the macrokinetics of this regime by starting from steady-state equations of type (8)–(10). The problem consists in determining the linear velocity of polymerisation, the width and structure of the front, the temperature distribution, and the extent of reaction: this can be done by using the concepts and methods of the theory of thermal waves[25-29]. The basic assumption needed to arrive at an analytic solution of the system (9)–(11) is that the reaction is confined to a narrow region where the temperature T_m is a maximum. Allowance should also be made for the difference in thermal and physical properties between the initial mixture and the polymerised product, i.e. for the dependence of the thermo-physical properties of the system on the extent of reaction. This is not possible with existing methods of calculation.

In radical polymerisation under frontal conditions it is important to consider the presence of the gel effect. An attempt to allow for the gel effect by using empirical formulae is described in Ref. 60.

5. Optimisation of Technological Processes

Optimisation problems can be formulated from a macrokinetic description of the polymerisation process. Various optimisation criteria are possible: the only requirement is that the criterion should be consistent with well validated methods of calculating and predicting the behaviour of polymerisation reactors. To solve the optimisation problem we must allow for the changes in structural parameters and in physical and mechanical characteristics resulting from the polymerisation, because these characteristics determine the properties of the finished item of interest to the consumer. Work on these problems has only just begun. Thus some recently reported investigations[61-63] of the optimisation problem aimed to minimise the reaction time while maintaining externally controllable temperature gradients, extents of reaction, and radical temperature differences at all extents of reaction.

6. Determination of the Kinetic Characteristics

Failure to allow for the exothermic effects of the reaction, which give rise to variations in temperature, reaction rate, and extent of reaction over the reacting volume, can lead to serious errors in the kinetic description of the non-isothermal polymerisation process. The problem of the kinetics of setting of a phenol–formaldehyde resin, which has been discussed in the literature for many years, is a particularly good example: different workers arrive at contradictory conclusions on the main kinetic features of this reaction. Most of them assume the presence of a significant induction period, because the time dependence of the measured kinetic factor is S-shaped. However Basov and coworkers[64] studied the dependence of the observed induction period t_{ind} on the size of the reaction vessel in a series of experiments with flat vessels of variable thickness d. They observed a square-law dependence of t_{ind} on d, and the induction period vanished on extrapolation to $d = 0$. This means that the induction period is an apparent "non-isothermal" effect. When the experimental results are extrapolated to isothermal conditions the rate of poly-condensation becomes constant, and the induction period disappears.

One consequence of the development of the theory of non-isothermal polymerisation was the appearance of new methods of determining the kinetic model of the process and of calculating the kinetic parameters. The most rigorous solution of this (inverse) problem relies on continuous measurement of self-heating against time. This is often done under conditions of uniform heating, when temperature distributions within the reaction volume can be ignored.

For polymerisation under adiabatic conditions we can write[65,66]

$$C\rho \mathrm{d}T/\mathrm{d}t = -Q\mathrm{d}M/\mathrm{d}t, \tag{14}$$

where M is the concentration of monomer. If the ratio $Q/C\rho$ is constant this simplifies to

$$M_0 - M = (T - T_0)C\rho/Q, \tag{15}$$

where M_0 and T_0 are the initial concentration and temperature respectively. When the reaction is complete we have

$$\Delta T = T_\infty - T_0 = M_0 Q/C\rho. \tag{16}$$

Thus the fact that the self-heating $\Delta T = T_\infty - T_0$ is independent of T_0 and is proportional to the initial monomer concentration M_0 confirms on the one hand that polymerisation is proceeding under truly adiabatic conditions and on the other hand that the ratio $Q/(C\rho)$ is constant.

The extent of reaction can be expressed in terms of the dimensionless parameter $\eta = (M_0 - M)/M_0$, or

$$\eta = (T - T_0)/(T_\infty - T_0). \tag{17}$$

For a reaction of the n-th kinetic order we have

$$-\mathrm{d}M/\mathrm{d}t = k_0 M^n \exp(-E/RT). \tag{18}$$

In this case Eqns. (14)–(18) allow us to express the rate of change of temperature as

$$(T_\infty - T)^{-n}\frac{\mathrm{d}T}{\mathrm{d}t} = k_0 (T_\infty - T_0)^{1-n}\exp(-E/RT). \tag{19}$$

Thus a plot of $\lg[(T_\infty - T)^{-n}dT/dt]$ against $1/T$ should be a straight line from which the kinetic constants k_0, E, and n can be evaluated (in the case of n, by trial and error). This method has been used by several workers[63-73].

This simple procedure has been extended to more complex kinetic schemes[74-76]. We shall consider its application to radical polymerisation with full allowance for the three basic steps (initiation, chain growth, and chain breaking). The reaction is usually assumed to be quasi-stationary (rate of change of the concentration of macroradicals much smaller than their rate of formation and of disappearance, and rate of initiation equal to the rate of chain breaking). With this assumption the kinetics of radical polymerisation can be described by the expressions

$$-\mathrm{d}M/\mathrm{d}t = k_{\mathrm{eff}} I^{1/2} M \exp(-E_{\mathrm{eff}}/RT), \tag{20}$$

$$-\mathrm{d}I/\mathrm{d}t = k_{i0} I \exp(-E_i/RT), \tag{21}$$

where M and I are the time-dependent concentrations of monomer and of initiator, k_{eff} and E_{eff} are the effective kinetic constants of the polymerisation reaction ($k_{\mathrm{eff}} = k_{p0}(k_{i0}/k_{t0})^{1/2}$; $E_{\mathrm{eff}} = E_p + \frac{1}{2}(E_i - E_t)$; k_{i0}, k_{t0}, k_{p0}, E_i,

E_t, and E_p are the pre-exponential factors and the activation energies for the initiation, chain breaking, and chain growth reactions respectively).

If the reaction occurs under adiabatic conditions we can write

$$-Qm\mathrm{d}M=(C_1m_1+C_2m_2+C_3m_3)\,\mathrm{d}T \tag{22}$$

or

$$\mathrm{d}M/\mathrm{d}T=-C/Q, \tag{23}$$

where $C = C_1 + C_2m_2/m_1 + C_3m_3/m_1$, Q is the heat of the chain growth reaction, C_1, C_2, C_3 and m_1, m_2, m_3 are the specific heats and the masses of the reaction medium, the solvent, and the bulb respectively. In Eqn. (22) the thermal contributions of the initiation and chain breaking reactions are ignored because these reactions are weakly exothermic in comparison with the chain growth reaction.

Replacing M by the dimensionless parameter $\eta = (M_0 - M)/M_0$ we can re-write Eqn. (20) in the form

$$\mathrm{d}\eta/\mathrm{d}t = k_{\mathrm{eff}}\,(1-\eta)\,I^{1/2}\exp(-E_{\mathrm{eff}}/RT). \tag{24}$$

By introducing the simplifying assumption that the concentration of initiator remains constant ($I = I_0 = \mathrm{const}$) we can write $k' = k_{\mathrm{eff}}I_0^{1/2}$, and the problem reduces to the vase of adiabatic polymerisation with a simple kinetic scheme. Tonoyan and coworkers[74] proposed a formula for the concentration of initiator which allows for its variation with temperature and time:

$$I=I_0\exp\{-k_{i0}t\exp(-E_i/RT)\}. \tag{25}$$

In this case Eqn. (24) becomes

$$\lg\left(\frac{\varepsilon_1}{T_\infty-T}\frac{\mathrm{d}T}{\mathrm{d}t}\right)+\frac{k_it}{4.6}\exp\left(-\frac{E_i}{RT}\right)=\lg k_0+\frac{1}{2}\lg I_0-\frac{E}{RT}. \tag{26}$$

Truly adiabatic conditions are not usually possible, and the solution of the inverse problem should take account of the transfer of heat to the surroundings. A thermographic method[77,78] has been proposed to evaluate the function $\varphi(\eta)$ in the case of simple kinetics. The same method is used in Ref. 37.

If temperature distribution over the volume of the reactor can be ignored the thermal regime of the reaction is given by the heat balance equation

$$C\rho\frac{\mathrm{d}T}{\mathrm{d}t}=Q\rho\frac{\mathrm{d}\eta}{\mathrm{d}t}-\alpha\frac{S}{V}(T-T_0) \tag{27}$$

with the initial conditions

$$t=0\quad T=T_{\mathrm{init}},\ T_0=T_{0\,\mathrm{init}},\ \eta=0. \tag{28}$$

From Eqn. (27) the rate of the non-isothermal reaction and the extent of reaction are found to be

$$\frac{\mathrm{d}\eta}{\mathrm{d}t}=\frac{C}{Q}\frac{\mathrm{d}T}{\mathrm{d}t}+\frac{\alpha(S/V)}{Q\rho}(T-T_0),\quad \eta=\frac{C}{Q}(T-T_{\mathrm{H}})+\frac{\alpha(S/V)}{Q\rho}\int_0^t(T-T_0)\,\mathrm{d}t. \tag{29}$$

Eliminating time as a parameter in Eqn. (29) we can evaluate the kinetic function $d\eta/dt = \varphi(\eta)$. If the semi-logarithmic plot of reaction rate against reciprocal temperature for a fixed η is linear we can determine the pre-exponential term and the activation energy. It is sometimes found that the activation energy varies with the extent of reaction. This effect may be associated with the increase in viscosity of the reaction medium. By carrying out non-isothermal polymerisation without temperature gradients we can convert the non-isothermal kinetic curves into isothermal curves, and thus simplify the treatment of the experimental results. Hence the kinetics of non-isothermal polymerisation are most conveniently investigated with special experimental arrangements to ensure this condition. The solution of the inverse problem outlined above in the presence of temperature distributions requires experimental measurement of the distribution and calculations on a computer.

IV. NON-ISOTHERMAL DEFORMATION OF SOLID POLYMERS

1. Cyclic Deformation

During the cyclic deformation of solid polymers heat is evolved as a result of the non-ideality of the elastic deformations, which causes some of the mechanical work done in the cycle to be irreversibly dissipated and converted into heat. If the properties of the material do not change within the cycle this work is given by the formula

$$A_\tau=\pi\varepsilon_0\sigma_0\sin\delta, \tag{30}$$

where ϵ_0 and σ_0 are the amplitude of the deformation and the stress respectively for a frequency ω, and δ is a characteristic of the material called the mechanical loss angle. It is important to note that δ is a function of temperature and frequency, and it can vary quite sharply within some ranges of these parameters. From the point of view of the present discussion we should also note the steep fall in elasticity and the increase in mechanical losses of polymers in the region of relaxation transitions (the most important of which is the glass transition). Sharp changes in mechanical properties and in δ are observed also as a result of phase transitions if the temperature rise produced by the deformation is sufficient to exceed the phase transition temperature.

Since the number of vibrations per unit time is $\omega/(2\pi)$, the energy A evolved per unit time during the cyclic deformation of polymeric materials is

$$A=\frac{\omega}{2\pi}A_\tau=\frac{\varepsilon_0\sigma_0}{2}\omega\sin\delta=\frac{\varepsilon_0^2\omega}{2}G'', \tag{31}$$

where G'' is a characteristic of the mechanical properties of visco-elastic materials called the loss modulus.

The values of δ and G'' for various polymeric materials in different physical states are listed in standard tabulations (see, for example, Refs. 2 and 79). We should stress that in every case $G'' > 0$, i.e. the deformation process is invariably dissipative. Formulae (30) and (31) apply both to solid and to rubbery substances. As in the cases considered above the rise in temperature is controlled by the transfer of heat to the surroundings, and the material constants which characterise the level of heat evolution are strongly temperature dependent, at least in some critical regions of temperature. Therefore, as has already been pointed out[80-83], this mechanical phenomenon is analogous to non-isothermal chemical reactions. The similarity extends to the critical effects: thermal explosion in the case of a chemical reaction and a similarly sharp and uncontrollable increase in temperature during cyclic deformation (leading to the destruction of the item or to the loss of its ability to withstand changes in shape.

Different regimes of temperature change are possible during cyclic deformation[80,84]. In the case of efficient heat exchange and moderate stresses we observe self-heating up to some equilibrium temperature which depends on the amplitude of the stresses[85] (since this amplitude

determines the intensity of the heat evolution). This is the "stationary" case, the most favourable mode of operation of plastics components, and is the mechanical analogue of a non-isothermal reaction proceeding under conditions far removed from the "thermal explosion" regime (for example, a polymerisation with a relatively small heat of reaction). The analogy can be extended to the manner in which the process comes to an end: the reaction stops by the depletion of reactants (in the absence of "topping up"), and the component is destroyed by the exhaustion of its mechanical durability.

The analogy between the thermal effects associated with cyclic deformation and those produced by a chemical reaction applies also under non-stationary self-heating conditions, resulting in an avalanche-like temperature rise followed by destruction of the sample (or component). The increase in temperature causes an increase not only in the heat transferred to the surroundings (as a result of the increased temperature difference) but also in the heat evolution within the sample, since the mechanical losses are greatest at softening (or relaxation transition) temperatures. If the temperature dependence of the heat evolution (dQ_+/dT) is more marked than that of the heat losses (dQ_-/dT) the temperature continues to rise up to the critical region where the material softens and resistance to deformation is lost.

These general cosiderations define the conditions of the transition from the non-stationary regime of temperature growth during cyclic loading to the stationary regime of isothermal deformation (though at a temperature higher than the initial temperature). The conditions are given[80-83] by the simultaneous solution of the two equations

$$Q_+ = Q_-; \quad dQ_+/dT = dQ_-/dT. \tag{32}$$

The solution of this system depends on the temperature (and frequency) dependence of the mechanical losses accompanying the cyclic loading of the particular polymeric material, on the size and shape of the sample, on the way in which the load is applied (since this determines the non-uniformity of the stress distribution, and therefore the rate of heat evolution), and on the heat exchange conditions. Some typical calculations of the critical parameters (i.e. some solutions of Eqns. (32) for various assumed types of loading) are given in the literature[84,86].

Thus studies of the non-isothermal cyclic loading of solid polymers indicate the existence of two basic non-isothermal deformation regimes: a "stationary" regime, leading to a "new" isothermal state in which the stable temperature level depends on the amplitude of the applied stresses, and non-stationary regime characterised by the onset of a critical self-heating ΔT_K at a well-defined amplitude of the applied stresses. It is important to note that the value of ΔT_K is almost independent of the external conditions (loading regime and heat exchange conditions), and in this sense it is a characteristic constant of the material. Critical values of the self-heating (ΔT_K) and of the stresses for many constructional polymers have been tabulated[84].

The stationary and the non-stationary heating regimes described above for samples undergoing cyclic deformation can be interpreted as "pure" manifestations of the heating effects arising from specific combinations of a dissipative factor and a heat transfer factor. At very high levels of applied stress the self-heating can be small if the sample is destroyed before reaching very high temperatures. Another important non-extreme case is a continuous slow rise in temperature—or even a rise followed by a fall in temperature—without reaching a stationary regime. This behaviour is usually associated with changes in the mechanical (visco-elastic) properties of the material during deformation as a result of concomitant physical or chemical structural processes[87-91].

2. Uniaxial Strain

The evolution of heat during the non-cyclic deformation of solid polymers in the uniaxial strain regime reflects the specific features of the molecular mechanism responsible for the structural changes accompanying the deformation. These changes are invariably accompanied by heating effects[92-99] which are a measure of the deviation of the material under study (under the particular deformation conditions) from the "ideal elastic body" or "ideal rubber" models which describe the purely energetic or entropic mechanisms of reversible deformation. In extreme cases the structural changes can lead to oriented crystallisation, with its accompanying thermal effect[100].

Heat evolution of this type has relatively little effect on the way in which the polymer deforms, because the temperature dependence of the mechanical properties of the material in a single physical (or relaxation) state is relatively weak: in other words, the "feedback" effect which plays a crucial role in most non-isothermal processes is absent in this case. Large effects can be expected if the rise in temperature produced by the heat evolved during deformation is sufficient to bring the sample to a transition region where the properties of the polymer are changing rapidly, thus affecting the subsequent deformation. This behaviour is most clearly seen when the temperature of the glassy sample rises to the glass transition temperature T_g. The mechanism of the stretching process changes radially above T_g. The most important aspect of this "devitrification" effect is the necking down of the sample, i.e. the sudden transition from a non-oriented to an oriented state[102], which occurs whether the devitrification takes place under isothermal conditions by an increase in the free volume[101] or whether it is due to a rise in temperature above T_g. The rapid increase in molecular mobility above T_g contributes to the relaxation processes and produces a sudden decrease in the rate of heat evolution.

The way in which this process develops depends on a number of factors: the ratio of the intensity of heat evolution by the mechanical deformation of the rigid polymer to the rate of heat transfer to the surroundings, the compliance (ability to store elastic energy) of the neck or of the yielding sections of the test piece, and also the strength of the polymer. In the simplest and most obvious case the local heating in the necking region, which can be as high as several tens of degrees, leads to a stationary necking down regime[98,103,104].

We shall not attempt to compare alternative mechanisms of the necking down effect, or to discuss the possibility of neck formation under strictly isothermal conditions (which is well established, and suggests that the mechanism of this phenomenon is not necessarily thermal[102,105]). For our present purpose we only need to mention the relevance to the set of phenomena considered here of a non-isothermal mechanism of neck formation (more strictly, the quasi-isothermal mechanism, analogous to the stationary cyclic loading process discussed in the previous section). This mechanism depends on intense, local heat evolution, temperature rise, and a sudden increase in molecular mobility before reaching devitrification conditions (and therefore before reaching the possibility of changes in

physical state, which tend to suppress the mobility by assisting molecular orientation of the polymer). This thermal mechanism of neck formation causes stationary propagation of the neck over the sample at a rate equal to the rate of deformation until the whole of the sample is included in the neck.

These are not the only non-isothermal phenomena during uniaxial stretching. Under certain conditions[106,107] the stationary neck propagation mechanism (which can be likened to a stationary chemical reaction) is replaced by an oscillatory stretching mechanism which has no analogues among the polymerisation processes but is similar to the oscillatory regimes observed in chemical reactions[108].

The critical condition for the appearance of self-oscillations during stretching under non-isothermal conditions is a particular combination of mechanical properties (which determine the elastic and the dissipative properties of the specimen being deformed) and heat-transfer properties (which determine whether the temperature of the polymer can rise above T_g). In these circumstances the stored elastic energy is suddenly released, leading (after a period of elastic deformation up to the critical strain) to an explosive growth in the rate of deformation when the local temperature in the necking region reaches T_g, and to a very sharp increase in the compliance of the polymer in this region. The increase in temperature causes a decrease in stress and an equally sharp decrease in the rate of heat evolution. The length of the high-temperature region of the sample is limited by the low thermal conductivity. Therefore, after the stress has collapsed and the cold zone has been reached we expect a new stage of slow stretch in the elastic region with accumulation of elastic energy in the easily deformed parts of the kinematic circuit and with a slow increase in stress until a new "collapse" is produced by the strong non-isothermal effect. The repetition of these phenomena produces a periodic (oscillatory) mechanism of non-isothermal stretching, and the resulting neck develops a clearly defined "banded" structure.

The direct link between the peaks in the local rate of deformation, the changes in stress during elongation, and the surges in heat evolution (with corresponding sharp changes in temperature) has been confirmed by direct observations[98,99,109]. This is a convincing illustration of the non-isothermal nature of the effect, involving all the aspects of the phenomena with which the present review is concerned: the role of heat evolution as an internal property of the system, the strong temperature dependence of the parameters which determine the rate of heat evolution (feedback effect), and the crucial importance of heat transfer to the surroundings.

These experimental facts on the oscillatory regime of neck formation during the stretching of polymers, and their physical treatment in terms of the general model of non-isothermal deformation processes, have been discussed in the literature[106,107] and formulated mathematically[110].

3. External Friction

External friction is a typical dissipative effect, limited by the transfer of heat to a solid support or to the surrounding atmosphere, and originating from heat evolution by surface friction. The system usually reaches an equilibrium temperature (corresponding to equality of heat evolution and heat extraction) which can be much higher than the initial temperature. This phenomenon is well understood, including the extreme temperature increases (similar to the "thermal explosion" in chemical reactions) which lead to the melting of metal bearings under excessive load. Equally catastrophic results can be produced in bearings made of polymeric materials by heat evolution and uncontrolled temperature rise, especially since the poor thermal conductivity of polymers allows the temperature of the friction surface to increase by a large amount. This can lead to true melting of the surface layer or to substantial softening (loss of hardness and strength) if the polymer cannot melt.

The critical self-heating is analogous to the uncontrolled temperature rise during cyclic deformation, and it involves essentially the same mechanism, since the frictional resistance to slip is due in part to periodic visco-elastic deformations of the polymeric material. The combined measure of the resistance to deformation and of heat evolution by friction is the coefficient of friction, which depends on the slip velocity, to some extent on the load, and on the temperature, and which is found to increase very rapidly near the melting (or softening) temperature of the polymer, leading in extreme cases to a transition from external slip to viscous flow in a layer of very high viscosity[111-115]. A mathematical theory of this phenomenon has been developed[116].

Melting effects as a result of heat evolution by external friction in polymers are not always unfavourable in polymer technology. In the initial stages of polymer treatment processes, when the material must be converted into a state capable of flowing, heat evolution by strong external friction can contribute very significantly to the temperature rise of the charge. This effect is especially marked in extrusion, because the conversion of the solid polymer into a flowing state in the first few turns of the worm conveyor occurs mainly by the heat of external friction.

The reverse transition—from a flowing to a rigid state—occurs in parallel with the flow of the polymer, and it plays an important role in the feed channels of moulding machines and during the filling of the mould. In this case the flowing material is cooled at the walls of the channel, forming a solid layer of increasing thickness. However the continuing flow causes dissipation in the layer, maintaining the flow properties and hindering the growth of the solid layer. Thus we have a complicated interaction between the increase in viscosity due to heat transfer to the cold walls of the channel and the resulting increase in dissipation, which limits the increase in viscosity. This technologically important and complex problem—the growth of solid layers under non-isothermal conditions—has been discussed by many workers[117-121]. The most convincing results were obtained in a recent study[122] of a material with well characterised thermo-physical properties (polyethylene), which clearly established the basic features of the phenomenon. In particular it was shown that under certain conditions the boundaries of the solid layers in a plane-parallel channel remain almost parallel as a result of the interplay of these effects. On the whole, the thickness of the solid layer increases with t^m (where t is time). The exponent is $m \simeq 0.4$, but its exact value depends on the properties of the material. The method of calculation used in Ref. 122 can be applied to other materials of technological interest.

The transition of the melt from a flowing to a rigid state occurs under non-isothermal conditions, and is due to crystallisation of the polymer. Therefore it should not be confused with the basically different transition from a flowing to a rigid state discussed in Refs. 123–126, which

occurs primarily under isothermal conditions and is due to relaxation phenomena. We note that crystallisation during flow can occur under isothermal conditions under the influence of orientation effects, which cause a shift in the temperature of the phase transition[127-131]. This mechanism can also produce a transition from a flowing to a rigid state, but in contrast to the non-isothermal mechanism discussed above it does not involve the two features common to the whole groups of mechanical phenomena discussed in this review: heat transfer and heat evolution by deformation.

V. NON-ISOTHERMAL FLOW

1. Dissipative Flow and Non-isothermal Viscometry

One of the most important aspects of the deformation of flowing systems is the evolution of heat. The deformation is non-isothermal for a number of reasons. The most important is the viscous or dissipative evolution of heat at high rates of deformation in highly viscous systems. In rheologically complex systems the thermal effects are accompanied by structural changes at various levels. In the deformation of reactive media additional heat can be evolved by chemical reaction (for example, polymerisation).

In the non-isothermal flow of liquids the resistance to deformation does not vary monotonically with flow rate. This is easily explained, for example, in the simple case of the shear flow of a Newtonian liquid, for which

$$\tau = \mu(T)\dot{\gamma}, \tag{33}$$

where τ is the stress, $\dot{\gamma}$ is the shear rate, and $\mu(T)$ is the temperature-dependent viscosity. The viscosity coefficients of many polymer systems (both solutions and melts) are accurately known and have been tabulated systematically[2,79,132-135].

In the isothermal case τ increases with $\dot{\gamma}$ according to formula (33). However in the non-isothermal case the resistance to deformation increases only as long as the self-heating is small. At higher strain rates the intensity of the dissipative evolution of heat increases, the self-heating becomes more pronounced, and the viscosity decreases. When the temperature dependence of the viscosity is non-linear this factor becomes even more important, and τ begins to decrease. The variation of the dissipative heat evolution $q(T)$ with temperature depends on the flow conditions[136]. Since

$$q(T) = \tau\dot{\gamma}, \tag{34}$$

it follows that for a constant kinematic parameter $\dot{\gamma}$ (flow rate under forced flow conditions, or velocity of the moving boundary under Couette flow) we can write

$$q(T) = \dot{\gamma}^2\mu(T). \tag{35}$$

In this case $q(T)$ decreases with increase of temperature.

On the other hand if we keep constant the dynamic parameter τ (the drop in pressure, or the driving force at the moving boundary) we have

$$q(T) = \tau^2/\mu(T). \tag{36}$$

In this case the evolution of heat increases with temperature, and the temperature of the liquid rises continuously as a result of thermal feedback[136]. This is the essential analogy between the progress of a chemical reaction in a viscous liquid and the non-isothermal flow of that liquid.

These features are observed in a number of dissipative phenomena[136-139]. The most fully investigated is the hydrodynamic thermal explosion[136], which can be realised experimentally in a rotating viscometer[140]. This is essentially a thermally unstable flow situation, in which the heat generated by internal friction cannot be extracted through the walls of the vessel. This produces a gradual increase in temperature and in the angular velocity of the rotor (for a constant applied torque).

Specific dissipative phenomena are possible during the forced flow of polymers in a tube of finite length. The convective flow of heat through the outlet cross-section and the limited residence time of the liquid in the tube are analogous to the consumption of reactant in a chemical reaction. However the non-linearity of the dissipative (heat evolution) function does not lead to a hydrodynamic thermal explosion in this case: it produces a sharp, discontinuous transition from a low-temperature and low-flow stationary regime to a high-temperature regime, and *vice-versa*, as the pressure drop is gradually changed. The critical conditions for the forward and the reverse transition are not identical (hysteresis effect). This phenomenon has been called hydrodynamic thermal ignition and extinction[138].

Interesting effects are observed from the interaction of dissipative heat evolution and elastic deformation. Self-oscillating flow regimes are possible for some combinations of the characteristic times of heat evolution, heat transfer, and elastic deformation, leading to relaxation fluctuations in stress, temperature, and heat evolution function. A wide variety of different flow regimes can be induced by different ratios of the characteristic times[139].

An important practical application of the theory of non-isothermal flow in viscous liquids has been the development of the non-isothermal method of studying rheological properties[141-143], which relies on the self-heating of the liquid in order to measure viscosity at different temperatures. The non-isothermal method consists in analysing the experimentally measured time-dependent changes in the temperature of the liquid $T(t)$ and in the speed of the rotor of a rotating viscometer $n(t)$ for a constant applied torque M = const, or by measuring $M(t)$ for n = const. This procedure ensures uniform heating of the liquid over the entire volume and minimises heat transfer to the surroundings. Under quasi-stationary hydrodynamic conditions, which exist for relatively high values of the Prandtl criterion $\mathrm{Pr} = \mu/(\rho a) \gg 1$ (where μ is the viscosity, ρ is the density, and a is the thermal diffusivity coefficient) we can determine the variation of the effective viscosity with temperature and with shear stress from experimental plots of $T = T(t, M)$ and $n = n(t, M)$.

This approach is specially useful for determining the variation of viscosity with temperature T and with the extent of reaction of the polymerising mass η, whose value (together with the rate of polymerisation $d\eta/dt$) can be obtained from the heat balance equation[77,78].

2. Non-isothermal Polymerisation in Flow Reactors

Macro-kinetic studies of flow reactors have progressed slowly in recent years. The special features of these reactors (outflow of the reaction products and limited residence time in the reactor) do not allow direct application of the theory of thermal explosions, as was done for batch reactors. Nevertheless the methods of this theory can be applied successfully to an analysis of the thermal

regimes. Typical of this approach are a number of studies[8,144,145] of the course of exothermic reactions in reactors assumed to have ideal mixing, ideal displacement, or displacement with longitudinal transport. The system of equations which describes the thermal regime in these reactors differs from the equations for batch reactors only in having additional terms for the rate of removal of heat and of the reaction products of the flow. In the simplest case of a single exothermic reaction in an ideally mixed flow reactor the equations can be expressed in the dimensionless form[145]

$$\gamma\, d\theta/dt = \exp[\theta/(1+\beta\theta)]\varphi(\eta) - \theta/\varkappa, \qquad (37)$$

$$d\eta/dt = \exp[\theta/(1+\beta\theta)]\varphi(\eta) - \eta/Da,$$

$$\theta = \frac{E}{RT_*^2}(T-T_*), \quad \tau = k_0 e^{-E/RT_*}t, \quad \eta = \frac{M_0 - M}{M_0}, \quad \beta = \frac{RT_*}{E},$$

$$\gamma = \frac{C}{Q}\frac{RT_*^2}{E}, \quad \varkappa = \frac{Q\rho}{\alpha_*(S/V)}\frac{E}{RT_*^2}M_0 e^{-E/RT_*},$$

$$Da = \frac{V}{\omega}k_0 e^{-E/RT_*}, \quad \alpha_* = \alpha + \frac{C\rho}{S}\omega. \qquad (38)$$

In these equations T_* is a scaled temperature defined as

$$T_* = (\alpha S T_0 + C\rho\omega T_{in})/(\alpha S + C\rho\omega), \qquad (39)$$

where T, T_0, and T_{in} are the temperatures of the material, of the surroundings, and of the incoming flow respectively, α_* is the effective heat transfer coefficient (allowing for all the heat losses), ω is the volume flow rate, $\varkappa$ is the Semenov criterion, and Da is the Damkeler criterion.

The most important parameters are the Semenov criterion (which expresses the ratio of the characteristic times for the removal and the production of heat) and the Damkeler criterion (which expresses the ratio of the residence time to the reaction time).

In the case of ideal displacement reactors the convective flows of heat and of matter in the longitudinal direction are important, and they give rise to a boundary condition at the inlet of the reactor. In displacement reactors with longitudinal transport we must introduce additional second-order terms for the effect of the diffusional flows of heat and of matter in the flow direction, and these give rise to a boundary condition at the outlet of the reactor.

A unique feature of polymerisation in flow reactors is the possibility of several stationary states. Zel'dovich[146,147], and, later, van Heerden[148], showed that the stable low-temperature and high-temperature regimes of an ideally mixed reactor depend on the ratio of the Semenov and the Damkeler parameter. The transition from the low-temperature to the high-temperature regime (ignition and extinction), and *vice-versa*, shows hysteresis: the critical conditions for the forward and the reverse transition are not usually identical. Similar features are observed in an adiabatic displacement reactor of finite length[149-151]. In the presence of lateral heat exchange the number of possible stationary states increases to five[152,153].

The existence of a low-temperature (quasi-isothermal) and a high-temperature (quasi-adiabatic) regime is demonstrated in Ref. 154 for an ideally mixed reactor and in Ref. 149 for a displacement reactor. In both these papers the sharp change from one regime to the other is ascribed to changes in the criteria describing the external conditions of the process. Beskov and coworkers[155] also point out the possibility of two regimes in a displacement reactor, but they ascribe it to changes in the internal criterion γ, i.e. to degeneracy of the critical conditions[38,39].

The general formulation of the non-stationary problem with allowance for longitudinal transport is discussed in Refs. 156 and 144. The results obtained are highly relevant to our understanding of the validity of our current models of flow reactors (ideally mixed, or displacement).

The thermal regimes of flow reactor operation have so far been treated as the displacement of an elementary volume in space. Maksimov and coworkers[156] attempted to allow for a radical velocity distribution in the liquid in the form of a Poiseuille profile, which causes a marked spread of residence times. The result is a "saddle-shaped" temperature and extent of reaction profile, and also the extension of the high-temperature (quasi-adiabatic) regime to include conditions in which the mean residence time is smaller than the induction period of the adiabatic thermal explosion.

Numerical solutions[157,158] of the equations describing polymerisation in a tube reactor have shown that the initial parabolic velocity profile becomes "stretched" in the axial direction if allowance is made for the variation of viscosity with temperature and concentration.

The residence time of the charge in the reactor depends on the viscosity. As the viscosity increases (due to the formation of products) the dissipative self-heating of the charge becomes increasingly important. This factor determines the conditions for changes in regime, and it can produce novel hydrodynamic effects. Even in the absence of chemical heat evolution we can find critical hysteresis effects due to the non-linearity of the variation of viscosity with temperature[138] or with extent of reaction[159]. These phenomena are reflected by discontinuous changes in flow rate with applied pressure. The increase of viscosity under forced flow can also result in blocking of the channel[159].

The interaction of dissipative and chemical heat evolutions is discussed in Refs. 160–164. Various "hydrodynamic", "chemical", and "intermediate" regimes have been demonstrated, and the number of possible stationary states of the system has continued to increase.

A full mathematical analysis of polymerisation in a flowing medium is given in Ref. 164, where the problem is treated as a one-dimensional case of the viscometric flow between two rotating cylinders separated by a narrow gap. Of course, this simple model can only reveal the principal effects produced by non-isothermal flow during the polymerisation of a liquid. In this model formulation it is assumed that the variation of the viscosity μ with reciprocal temperature and with extent of reaction is experimentally known:

$$\mu = \mu_0 \exp(U/RT + B\eta), \qquad (40)$$

where U is the activation energy for viscous flow, R is the gas constant, and B is a constant which allows for the effect of the reaction on the viscosity of the charge, and hence on the intensity of the dissipative processes. It is assumed that U is independent of η.

A full formulation of the problem includes the kinematic equation for the distribution of velocity in the gap, the equation for the temperature distribution with allowance for the dissipative factors and for the heat transfer conditions at the walls of both cylinders, and the kinetic equation for η, allowing for the strong temperature dependence of the reaction rate. We note that η occurs in formula (40) as well as in formula (4), i.e. there is a complex interaction between the basic factors (temperature, flow rate, and rate of reaction), which is typical of the class of non-isothermal problems considered in this review.

A study[164] of several variants of the solution of this model problem has shown that the presence of dissipative heat sources (associated with the flow of the charge) assists the transition to a flow regime similar to the

hydraulic thermal explosion, i.e. to a sudden, uncontrolled decrease in viscosity and increase in the speed of rotation (if the torque applied to the rotating cylinder is kept constant) or decrease in torque (if the speed of rotation is kept constant). However it is important to note that if we fix the angular velocity of the rotating cylinder and we ignore the heat of the chemical reaction we always arrive at a stationary flow regime[160]. The role of the parameter B in formula (40), which allows for the effect of the reaction on the dissipation by viscous flow, is most important in flow regimes which fall short of the thermal explosion conditions. In this case the parameter B (i.e. the effect of the extent of reaction on the viscosity of the system) determines the maximum self-heating and the change in extent of reaction with time.

In spite of the great practical importance of a combined study of non-isothermal flow and chemical reaction the number of publications in this area is relatively small. Studies of this type are only just beginning, and existing results are limited to a few special model systems. These results show that the effects are far from trivial, but they cannot be applied directly to real technological situations or even to laboratory experiments.

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The number of non-isothermal effects in the chemistry and mechanics of polymers is vast. Their basic qualitative features in various regimes of polymerisation and deformation are now well recognised, and the most important effects produced by non-isothermal regimes have been described. However the work so far has been confined to observations in the laboratory. Yet, most industrial processes in polymer technology occur under essentially non-isothermal conditions. The need is quite obvious, but so far it has had very little effect on the general approach to non-isothermal processes because of the great complexity of an adequate quantitative treatment of the interplay of dissipation, deformation, and heat transfer phenomena. Only recently, with the development of appropriate theoretical models and computational techniques, have solutions of the model problems been obtained. Further developments in this direction must remain the main objective of quantitative studies of non-isothermal industrial processes for the production and application of polymeric materials.

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Progress in the Theory of Acids and Bases†

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Published data on the acid-base properties of organic substances in the gaseous phase have been reviewed. The proton affinity (PA) of bases is taken as the enthalpy of the gaseous reaction $M + H^+ \rightarrow MH^+$, with the opposite sign, and the basic strength of the bases (GB) is taken as the change in the standard free energy of this reaction (again with opposite sign). Correspondingly, the acidity in the gaseous phase is taken to be the enthalpy of the reaction $AH \rightarrow A^- + H^+$ or the change in the standard free energy of this reaction.
The dependence of the acid strength and base strength in the gaseous phase on the structures of the molecules of the acids and bases has been examined, and the lack of agreement between the observed facts and the classical electronic interpretation based on the inductive and mesomeric effects of the groups has been discussed. Attention has been drawn to the change in the acid-base properties of organic molecules on going from the gaseous to the liquid phase, and the energetic effects of the solvation of the molecules and ions have been examined.
The bibliography contains 78 references.

CONTENTS

I.	Introduction	814
II.	Principles of the experimental methods	815
III.	Basic strength in the gaseous phase	817
IV.	Ratio of the basic strengths in the gaseous and liquid phases	820
V.	Acid strength in the gaseous phase	823
VI.	Summary	825

I. INTRODUCTION

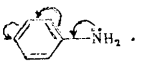
The modern electronic theory of organic chemistry, developed in the early nineteen-thirties on the basis of the classical theory of chemical structure, uses an electronic description of the structure of molecules and their reactivity[1].

The description of the structure has two sources and, correspondingly, two languages. The first is the theory of electronic effects (inductive and mesomeric), developed mainly by the efforts of the English school of chemists, and the second is quantum chemistry. The establishment of a satisfactory correspondence between these two descriptive systems was the greatest achievement of theoretical organic chemistry.

The electronic theory of *reactivity* has not reached this high level. The situation is better in the theory of radical reactions. The free valency indices and the energy of homolytic bond rupture can be calculated theoretically and made the basis of an examination. In the theory of ionic reactions, an important role is played by a fundamental principle: "nucleophilic reacts with electrophilic". Although there are exceptions to this principle, it works well in the great majority of cases. The determination of the degree of nucleophilic or electrophilic character of molecules and their fragments and complexes has therefore become an important task of theory. This degree of nucleophilic or electrophilic character is not equivalent to the distribution of the effective charges on the atoms, which can be calculated theoretically. Here, therefore, it is necessary to resort to the use of hypotheses and ideas constructed on the basis of so-called common sense. They appear to be reasonable, although in fact they are often somewhat doubtful. These hypotheses and ideas have in fact been accepted without proof as the only possible translation of the familiar regular features of the classical theory of chemical structure into the language of electronic theory. Since there has been no doubt that the classical theory adequately describes objective reality, these hypotheses have acquired the appearance of principles.

This applies particularly to the acid–base properties of substances, that is to proton transfer reactions. These reactions represent the simplest illustration of the principle "nucleophilic combines with electrophilic". This will therefore be the subject of the subsequent discussion, which begins with several examples of well known facts and their explanations to which we have become accustomed and whose possible revision we have not considered.

First example. The long familiar fact that the base strength of ammonia decreases on the successive attachment of phenyl groups, that is the series $NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH > (C_6H_5)_3N$, has always been explained by stating that in aniline, the unshared pair of electrons is partly transferred to the ring (+*M*-effect):



The mesomeric stabilisation of the base and the partial positive charge on the nitrogen are the factors responsible for the decrease in the base strength of aniline compared with ammonia, where these effects are not found. In diphenylamine, which has two phenyl rings, this effect is stronger, and triphenylamine is not basic at all. All appears sufficiently convincing and clear!? It is not quite so clear, however, why the resonance effect in the aniline molecule should produce such a marked decrease in the proton affinity of the molecule that aniline becomes a much weaker base than ammonia.

Second example. It is well known that pyridine is a much weaker base than ammonia and aliphatic amines. The lower base strength of pyridine has been attributed to the nature of the hybridisation of the unshared pair of electrons of the nitrogen atom. Its hybrid orbital has more *s*-character than in the case of ammonia and amines. In

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pyridine the hybridisation is sp^2, and in ammonia and amines sp^3. Since s-electrons are more firmly bound to the nucleus of the atom, the basic strength decreases with increase in the s-component[1]. Again, all appears logical. Not altogether, however! Why can it be assumed that the greater strength of attachment of the unshared pair to the nucleus alone can produce a much smaller proton affinity of the molecule? The attachment of a proton to two comparable molecules leads to extensive and different changes in their entire energetics, which primarily determine the magnitude of the relative proton affinity! Until recently, this has not been taken into account.

Third example. The introduction of methyl (and in general alkyl) groups in the series $NH_3 < CH_3NH_2 < (CH_3)_2NH$ leads to an increase in base strength, which we readily attribute to the $+I$-effect, that is the positive inductive effect of the methyl groups. On going from dimethylamine to trimethylamine, however, the basic strength decreases: $(CH_3)_2NH > (CH_3)_3N$ ($pk_{a(H_2O)}$ 10.77 and 9.80 respectively). To explain this anomaly, Brown[2] proposed his B-strain hypothesis. Later, under the influence of modern ideas, Condon[3] attributed it to be a change in solvation. In either case, special additional hypotheses were introduced, the aim of which was to save the *a priori* view of the decisive role of the $+I$-effect of the methyl groups.

Fourth example. The acidity of alcohols. We are accustomed to the fact that trimethylcarbinol is an incomparably weaker acid than ethanol. Alcohols can be arranged in the following order of acid strength[4]: $H_2O > CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3COH$; $H_2O > CH_3OH > C_2H_5OH > C_3H_7OH > C_4H_9OH$..... These series we explain without strain in terms of the inductive $+I$-effect of the alkyl groups. Clear and obvious! Really!? In exactly the same way we used the $+I$-effect to explain the course of the change in the acid strength of the carboxylic acids ($pK_{a(H_2O)}$ values in parenthesis): HCOOH (3.75) $>$ CH_3COOH (4.76) $>$ C_2H_5COOH (4.87) $>$ C_3H_7COOH (4.82) $\geqslant$ C_4H_9COOH (4.86) $\geqslant$ $C_5H_{11}COOH$ (4.86), and the $-I$-effect to explain the change in the strength of the halogenoacetic acids: FCH_2COOH (2.57) $>$ $ClCH_2COOH$ (2.86) $>$ $BrCH_2COOH$ (2.90), recalling that the electronegativities of the halogens decrease in the familiar order: F (4.0) $>$ Cl (3.0) $>$ Br (2.8).

These facts, which can easily be multiplied, are apparently fairly well interpreted by theory. If we were not convinced of this, we would not tell the students. The trouble is not that our arguments are not sufficiently logical. The trouble is that many of the facts which we can explain so successfully in fact are incorrect (in the context in which they are interpreted). This means that our explanations are also incorrect.

To anticipate, it may be said that this error has arisen because absolutely correct results on the measurement of acid or base strengths in the liquid phase have always been assigned only to the actual molecules of the substance being studied. In fact, however, these data should be related to the system consisting of the molecules of the substance being studied and the surrounding molecules of the medium. The acid–base properties of the actual molecules of the substance — outside the medium —are often quite different.

The lack of correspondence between our explanations and the data being explained and the actual state of affairs became clear with the development of high-pressure mass spectroscopy and, somewhat later, ion-cyclotron resonance spectroscopy. These methods made it possible to study the properties of molecules in the gaseous phase, that is when they are not distorted by the influence of surrounding molecules. It is the properties of the molecules in the gaseous and not the liquid phase that must be related to their electronic structure, various electronic effects, etc; in the liquid phase the distortions produced by the environment may be very great.

Here it should be specially stated that the subsequent treatment will deal not with any one or even several studies but with a large number of studies by various workers. Thus the data presented below are now firmly established. Reviews of the new results have been published, for example by Agami[5], Taft[6], and Kebarle[7].

II. PRINCIPLES OF THE EXPERIMENTAL METHODS

In high-pressure mass spectrometry[8–11], a pressure of $\sim 10-10^{-4}$ mmHg is used. Since ions in the gaseous phase are unstable (they disappear rapidly as a result of recombination or discharge on the walls), they must be continually created by the action of radiation. The apparatus must be constructed in such a way that it is possible, within the limited lifetime of the ions, to observe the interaction of the ions with molecules, leading to ion–molecular equilibrium.

The direct mass-spectrometric method of measuring the proton affinity of a molecule M involves the measurement of the appearance potential of the ion MH^+ as a fragment of the degradation of another molecule. From the appearance potential of the ion it is possible to calculate its enthalpy of formation, that is $\Delta H^\circ(MH^+)$, and hence the proton affinity (PA).

$$PA = \Delta H^0(H^+) + \Delta H^0(M) - \Delta H^0(MH^+)$$

The enthalpy of formation of hydrogen ions is calculated from the ionisation potential of atomic hydrogen, and the enthalpy of formation of the molecules M from thermochemical data. It is thus possible to calculate the proton affinity of the molecules M.

The method is one of the few giving absolute results. Its disadvantage is the frequently encountered difficulty of assigning the peaks to a specific ion and the occasional impossibility of obtaining a known given protonated species MH^+ of definite structure[12,13].

Soon after the first publications in this field[14,15], various methods were developed for determining the relative basic strength of molecules in the gaseous phase by high-pressure mass spectrometry. In all cases, a mixture of gases M_1 and M_2 is placed in the reaction cell. Positive ions are generated by electron collision, and the ratio of the concentrations of the ions M_1H^+ and M_2H^+ is measured by a suitable method. The results are used to calculate the equilibrium constant and standard free energy:

$$M_1H^+ + M_2 \rightleftarrows M_1 + M_2H^+$$
$$K = [M_2H^+] \cdot [M_1]/[M_1H^+] \cdot [M_2]$$
$$-\Delta G^0 = RT \ln K$$

To determine the relative acid strength of organic acids A_1H and A_2H in the gaseous phase by high-pressure mass spectrometry, various special methods for generating negative ions are used. An example is provided by the determination of the relative acid strength of two benzoic acids, developed in the University of Alberta in Canada[7]. A gas mixture consisting of the carrier gas methane

(5 mmHg), a weaker acid A_2H (0.050 mmHg), and a smaller quantity of a stronger acid A_1H is irradiated in a compartment by a beam of electrons (e); SO_2F_2 (0.1 mmHg) is added to the mixture for the formation of negative ions. The following principal reactions take place:

$$e + SO_2F_2 = SO_2F + F^-,$$
$$F^- + A_2H = HF + A_2^-,$$
$$A_1H + A_2^- \rightleftarrows A_2^- + A_2H.$$

The capture of an electron by sulphuryl fluoride is exothermic, since the electron affinity of fluorine is greater than the dissociation energy of the F–SO_2F bond. The reaction of the fluoride anion with A_2H is practically irreversible, since benzoic acids in the gaseous phase are much stronger than HF.

The resulting gaseous mixture is "withdrawn" continuously by a fast-acting vacuum pump into the compartment of the mass spectrometer, in which a high vacuum is maintained, and the usual separation according to mass is then carried out. This gives the ratio of the equilibrium concentrations of the ions A_2^- and A_1^- and hence the equilibrium constant:

$$K = [A_1^-] \cdot [A_2H]/[A_2^-] \cdot [A_1H].$$

K can be used to calculate the free energy of proton transfer ΔG°.

The generation of negative ions in the gaseous phase is often carried out using the radiolysis of methyl nitrite or NF_3 [24];

$$e + CH_3ONO = CH_3O^- + NO$$
$$e + NF_3 = F^- + NF_2.$$

The principles of ion-cyclotron resonance spectroscopy are as follows[16,17]. The ion MH^+ with charge q_1 and mass m_1, entering the uniform magnetic field H of the cyclotron, begins to move around a circular orbit of radius r^1, with velocity v_1 and angular frequency ω_1:

$$\omega_1 = v_1/r_1 = q_1H/m_1c.$$

On the applications of a variable electric field E_1 having a frequency ω, resonance occurs when $\omega = \omega_1$. The energy of the electric field is then absorbed, and the ions MH^+ obtain additional kinetic energy. The absorption of the energy of the electric field is reflected on the oscilloscope screen (scanning along the frequency scale ω) by an absorption peak.

To determine the relative proton affinity by the double resonance method, the ions M_1H^+ are generated by a suitable method in the cell of the ion-cyclotron spectrometer; these ions then react with the molecules M_2:

$$M_1H^+ + M_2 \rightleftarrows M_1 + M_2H^+.$$

On the application of two variable electric fields E_1 and E_2 having frequencies corresponding to the angular velocities ω_1 and ω_2 ($\omega_2 = q_2H/m_2c$), two signals are produced on the oscilloscope screen. From these two signals, using appropriate procedures, it is possible to calculate the proton affinity of the molecules M_2 relative to the molecules M_1.

A number of versions of the ion-cyclotron resonance method have been developed and are being used successfully, including the highly effective pulsed method[18–23]. In all cases the experiments are carried out at a low pressure ($p \leq 10^{-4}$ mmHg) and only at room temperature. The method makes it possible, however, to determine the relative concentrations of ions in situ, and has a high accuracy[21].

Basic strength in the gaseous phase is often expressed by the proton affinity of the molecule M, that is by the enthalpy of the reaction $M + H^+ \rightarrow MH^+$, taken with opposite sign: $PA = \Delta H^\circ(MH^+)$ kcal mole^{-1}. The acid strength in the gaseous phase is given by the enthalpy of the reaction $AH \rightarrow A^- + H^+$, again in kcal mole^{-1}. The higher the numerical value of the proton affinity, the stronger the base, and hence the weaker the acid. Strictly speaking, the negative enthalpy of the reaction $M + H^+ \rightarrow MH^+$ gives not the basic strength but the proton affinity. The basic strength GB (Gas-phase Basicity) is given by the change in the standard free energy of this reaction (again taken with negative sign). In practice, however, these quantities are equal or almost equal, since the entropy contribution here is very small. In fact, most published data have been obtained by relative measurements. Since proton transfer reactions are practically isentropic (free energies independent of temperature), the enthalpies for the equilibria measured are equal (or almost equal) to the free energies. Here the entropy term usually does not exceed 2 e.u., which at 298 K is 0.6 kcal mole^{-1}, and hence often lies within the limits of error of the measurement.

In most relative measurements, the standard used is ammonia, that is the equilibrium constant of the proton transfer: $NH_4^+ + M \rightleftharpoons NH_3 + MH^+$, is measured experimentally and used to calculate the free energy of proton transfer ($-\delta\Delta G^\circ$, kcal mole^{-1}) or the enthalpy of proton transfer ($-\delta\Delta H^\circ$, kcal mole^{-1}), which is equal to the latter.

In order to use these data to calculate quantities characterising the equilibrium $M + H^+ \rightleftharpoons MH^+$, namely the basic strength of the molecules $GB(M) = -\Delta G^\circ$ or their proton affinity $PA(M) = -\Delta H^\circ$, it is necessary to know the values of the basic strength and proton affinity of ammonia, that is the values of $-\Delta G^\circ$ and $-\Delta H^\circ$ for the equilibrium $NH_3 + H^+ \rightleftharpoons NH_4^+$. These values have been verified repeatedly, and it has been established that at 298 K they are: $GB(NH_3) = -\Delta G^\circ = 198 \pm 3$ kcal mole^{-1} and $PA(NH_3) = -\Delta H^\circ = 207 \pm 3$ kcal mole^{-1}.[8,9] The entropy term $T\Delta S^\circ$ includes a correction for the change in the symmetry on protonation (for ammonia, $\Delta S^\circ_{symm} = 0.82$ e.u.) and for the translational entropy of the ion H^+[$\Delta S^\circ(H^+) = 26.1$ e.u.].[25] ‡

Thus the published values of the basic strength of the molecules M are $GB(M) = -\Delta G^\circ = -\delta\Delta G^\circ + 198$ kcal mole^{-1}, and the values of the proton affinity of the molecules M are $PA(M) = -\Delta H^\circ = -\delta\Delta H^\circ + 207$ kcal mole^{-1}. These quantities naturally differ by approximately 9 kcal mole^{-1}.

Finally, it should be noted that both methods — high-pressure mass spectrometry and ion-cyclotron resonance spectroscopy — are based on the determination of the ions MH^+ or A^- from their masses. The question of the structure of the ion (protonation position) must be resolved independently by other methods, for example by isotopic substitution.

This entire field has developed comparatively recently. The first pioneer work of the late nineteen-fifties and early nineteen-sixties was carried out by Tal'roze[14]. Since 1965, after the work of Munson[15], the field began to develop rapidly. There are now five main centres in which proton transfer reactions in the gaseous phase are being studied.

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‡ A new and more accurate value, $-\Delta H^\circ(NH_3) = 202$ kcal mole^{-1}, has been reported[26]. If these data are confirmed, all the numerical values of the relative thermodynamic parameters, related to ammonia as standard substance, are altered by 5 kcal mole^{-1}.

1. Kebarle's group[7,10,24,27-31] in the University of Alberta, Edmonton, Canada. Here, high-pressure (~1 mmHg) mass spectrometry is used; the experiments are carried out at 600 K (at this temperature it is possible to avoid the formation of higher aggregates, which is unavoidable at the given pressure and room temperature). The group is studying the basic and acid strength of organic compounds in the gaseous phase and also the products of the attachment of neutral molecules to gaseous ions, which are regarded as a model of "supermolecules" — solvated molecules in the liquid phase.

2. Bowers, Aue, and coworkers[21,23,32] in the University of California at Santa Barbara. They use ion-cyclotron resonance at varying pressure. The experiment is carried out at room temperature and medium pressure ($\sim 10^{-4}$ mmHg). The group is studying the relative basic strength of organic compounds in the gaseous phase and the relationship between gas-phase and liquid-phase basic strengths.

3. McIver and coworkers[18,20,22,33-37] in the University of California at Irvine; this group is using pulsed ion-cyclotron resonance, suitable for accurate measurements at room temperature and low pressure ($\sim 10^{-6}$ mmHg). Both the basic and acidic properties of molecules in the gaseous phase are being studied. In the discussion of the results obtained in relation to the structure of the molecules and in comparison with the acid-base properties in the liquid phase, the group is cooperating with Taft, a well-known specialist in the correlation analysis of organic reactions, and Arnett, a specialist in the theory of solutions.

4. Beauchamp and coworkers[19,38] in the California Institute of Technology at Pasadena are studying the basic strength of organic compounds by ion-cyclotron resonance at low pressure ($\sim 10^{-6}$ mmHg) and room temperature.

5. Bohme and coworkers[11,39] at York University, Ontario, Canada are using a flow method to measure the rate constants and equilibria for proton transfer at room temperature.

The groups of McIver, Beauchamp, Bowers, and Aue have achieved a high accuracy in their measurements (±2 kcal mole^{-1}).

III. BASIC STRENGTH IN THE GASEOUS PHASE

1. Basic Strength of Various Simple Molecules in the Gaseous Phase[9,11]

Of the hydrides of the elements, ammonia has the highest proton affinity: $PA = 207 \pm 3$ kcal mole^{-1}.[9] In the first period of the periodic system, the lowest basic strength is naturally shown by methane §, so that it is possible to write the series (proton affinities in parentheses):

$$CH_4\ (126) < NH_3\ (207) > H_2O\ (165) > HF\ (137)\ .$$

In the second period, phosphine has the highest proton affinity: SiH_4 (146) < PH_3 (186) > H_2S (170) > HCl (141).

In the halogen series the basic strength of the hydrides increases from HF to HI:

$$HF\ (137) < HCl\ (141 \pm 3) \approx HBr\ (140 \pm 3) < HI\ (145)\ .$$

§ The proton affinity of methane was first measured by Tal'roze in 1958. The value obtained, $PA = 122$ kcal mole^{-1}, is close to the presently accepted value.

2. Basic Strength of Amines in the Gaseous Phase¶

a) Aromatic and heterocyclic amines

In contrast to all measurements in the liquid phase, in the gaseous phase aniline has been found to be a stronger base than ammonia, and only a slightly weaker base than methylamine. Diphenylamine has been found to be an even stronger base, of approximately the same strength as methylamine, and triphenylamine is the strongest of these bases, its strength being greater than that of methylamine[41]. Everything is reversed! Table 1 shows that the proton affinity of aniline in the gaseous phase is 8.9 kcal mole^{-1} greater than that of ammonia. According to other authors[42], the relative basic strength of aniline in the gaseous phase, that is the free energy of the proton transfer: $NH_4^+ + C_6H_5NH_2 \rightleftharpoons NH_3 + C_6H_5NH_3^+$, is slightly less than that, $-\delta\Delta G^\circ = 6.70$ kcal mole^{-1}.[6] According to these data also, however, aniline is a much stronger base than ammonia.

Table 1. Basic strength of various aromatic amines and ammonia in the gaseous phase and in water[41].

Basic strength	NH_3	$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
PA, kcal mole^{-1}	207	215.9[29]	~218	225>PA>218*
pK_a (H_2O)	9.27	4.58	0.9	<0

* Estimated by us from the data in Ref. 41.

Table 2. Basic strength of methylanilines in the gaseous phase and in water[29,30].

Basic strength	$C_6H_5NH_2$	$C_6H_5NHCH_3$	$C_6H_5N(CH_3)_2$
PA, kcal mole^{-1}	215.9	222.1	228.7
pK_a (H_2O)	4.58	4.85	5.06

Dzidic[41], who was the first to observe this phenomenon, wrote that the results which he obtained made it necessary to re-examine our ideas on the mesomeric effect. In fact, it is apparently necessary to re-examine not the idea of the mesomeric effect but the view that it plays a role in determining the basic strength of molecules.

An interesting feature is that the basic strength of N-alkyl derivatives of aniline in the gaseous phase increases with increasing replacement of the hydrogen atoms attached to nitrogen, in the same way as the basic strength increases in a liquid medium. Table 2 gives as an example the data for methylanilines[29,30]. In contrast to the previous case, the ratios of these quantities here have their usual values.

¶ The numerical values of the proton affinity given below are related to ammonia as standard [$PA(NH_3) = 207 \pm 3$ kcal mole^{-1}].

The usual change is also observed in the basic strength of aniline on hydrogenation. Table 3 shows that the basic strength of cyclohexylamine is greater than that of aniline both in the gaseous phase and in water[6,30]. According to Taft and coworkers[6,42], the free energy of proton transfer from the anilinium to the cyclohexylammonium ion

$$(C_6H_5NH_3^+ + \text{cyclo-}C_6H_{11}NH_2 \rightleftarrows C_6H_5NH_2 + \text{cyclo-}C_6H_{11}NH_3^+,$$

measured by ion-cyclotron resonance, is $-\delta\Delta G^\circ = 9.6$ kcal mole^{-1}. The order of the basic strength of heterocyclic bases was completely unexpected (Table 4). In water and in any other liquid medium, pyridine is incomparably weaker than ammonia, not to mention methylamine. In the gaseous phase, however, and hence by itself, its "intrinsic basic strength" is much greater than that of ammonia (by 18.9 kcal mole^{-1}) and is similar to that of dimethylamine. Thus the explanation of the lower basic strength of pyridine compared with ammonia, based on the type of hybridisation of the unshared pair of electrons of the nitrogen in pyridine, hangs in mid-air: pyridine is intrinsically a stronger base than ammonia.

Table 3. Basic strength of aniline and cyclohexylamine in the gaseous phase and in water[8,30].

Basic strength	$C_6H_5NH_2$	cyclo-$C_6H_{11}NH_2$
PA, kcal mole^{-1}	215.9	226.7
$pK_{a\ (H_2O)}$	4.58	10.64

Table 4. Basic strength of various heterocyclic bases in the gaseous phase and in water.

Basic strength	NH_3				
PA, kcal mole^{-1} (Ref.30)	207	214.15	225.6	228.7	231.5[21] 230.1
$-\delta\Delta H^\circ$ ($-\Delta H^\circ_{NH_3} = 0$) (Ref.30)	0	7,1	18,0	21.7	24.5
GB, kcal mole^{-1} (Ref.26)	198	205	216,9	220.4	221.5
$pK_{a(H_2O)}$	9.27	−0.27	5,23	11.27	11.22

At the same time, the influence of γ-substituents in the pyridine ring on the basic strength in the gaseous phase was studied. A good linear correlation is observed between the data for the gaseous phase and for water, with constants σ_I and σ_{R^+}[43]:

$$[\Delta H^0/\Delta H^0_0]^\dagger = 16{,}7\sigma_I + 10{,}3\sigma_R^+ \text{ (in the gaseous phase);}$$
$$\lg(K/K_0) = 5{,}15\sigma_I + 2.69\sigma_R^+ \text{ (in water).}$$

The basic strength in the gaseous phase is much more sensitive to change in the parameters σ, that is to the influence of substituents, than the basic strength in water. Water, as a medium for acid–base equilibria, shows a clearly defined levelling action compared with the gaseous phase.

† In log K units.

Thus the influence of substituents in the pyridine ring on the basic strength in both the gaseous phase and a liquid obeys the Hammett equation, and it seems that here there is no anomaly. It should be noted that quantum-chemical calculation by the CNDO/2 method also gives a similar result. Recently, Aue and coworkers[44] extended this correlation (with slight exceptions) to pyridine derivatives having substituents in the three positions, α, β, and γ.

b) Aliphatic amines[15,23,30,32,33,45]

A large number of studies have been devoted to amines. As alkyl groups are introduced into the ammonia molecule there is a monotonic increase in the basic strength in the gaseous phase, without any deviation for tertiary amines (Table 5). The basic strength in the gaseous phase also increases with increased length of the normal chain in the amine (Table 6). Moreover, it can be seen that, beginning from C_3–C_4, the increase in the basic strength in the gaseous phase becomes less marked. In water, all primary amines have the same basic strength, within the limits of experimental error.

Table 5. Basic strength of primary, secondary, and tertiary aliphatic amines in the gaseous phase and in water.

Basic strength	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$(C_2H_5)_3N$
PA, kcal mole^{-1}	207	218.4	224.9	229.1	221.1	230.1	235.8
GB, kcal mole^{-1} (Ref.26)	198	210.0	216.6	220.8	213.0	221.2	227.7
$pK_{a(H_2O)}$	9.27	10.62	10.77	9.80	10.63	10.93	10.87

Table 6. Dependence of the basic strength of aliphatic amines on the length of the normal chain in the gaseous phase and in water.

Basic strength	CH_3NH_2	$C_2H_5NH_2$	$C_3H_7NH_2$	$C_4H_9NH_2$	$C_5H_{11}NH_2$	$C_6H_{13}NH_2$
PA, kcal mole^{-1}	218.4	221.1	222.3	222.8	223.1	223.2
ΔPA, kcal mole^{-1}	11.0	3.1	1.2	0.5	0.3	0.1
GB, kcal mole^{-1} (Ref.26)	210.0	213.0	214.4	214.9	—	—
$pK_{a(H_2O)}$	10.62	10.63	10.53	10.60	10.63	10.64

The basic strength of amines in the gaseous phase also increases with branching in the substituent (Table 7). An interesting feature is that in aqueous solution the basic strength decreases in this case; this was attributed to *B*-strain. In general, however, the order of the change in the basic strength of amines agrees with the inductive $+I$-effect of the alkyl groups. It appears that here it is possible to retain the explanation based on this effect. This would be the case if there were no data on the acid strength of amines in the gaseous phase. To anticipate, it may be noted that the relative acid strength of alcohols and amines in the gaseous phase, which Brauman and Blair studied by semi-quantitative ion-cyclotron resonance[46,47] also

increases with increased number of alkyl groups on the nitrogen, the number of carbon atoms in them, and the degree of branching of their hydrocarbon skeleton, that is under the influence of the factors which led to an increase in the basic strength of amines:

$$(C_2H_5)_2NH > H_2O > NH_3;$$
$$(C_2H_5)_2NH > (CH_3)_2NH > NH_3;$$
$$C_3H_7NH_2 > C_2H_5NH_2 > CH_3NH_2 > NH_3;$$
$$(CH_3)_3CCH_2NH_2 > (CH_3)_3C{-}NH_2 > (CH_3)_2CH{-}NH_2 > C_2H_5{-}NH_2 > CH_3{-}NH_2 .$$

At the same time, naturally, the $+I$-effect also increases. According to all our ideas, however, the $+I$-effect cannot increase the acid strength; it can only decrease it. This means that the concept of the $+I$-effect cannot be used to explain the acid–base properties of amines. It is necessary to look for other ways of interpreting the experimental data.

Table 7. Dependence of the basic strength of aliphatic amines on the degree of branching of the carbon chain in the gaseous phase and in water.

Basic strength	n-$C_4H_9NH_2$	iso-$C_4H_9NH_2$	s-$C_4H_9NH_2$	t-$C_4H_9NH_2$
PA, kcal mole^{-1}	222.8	223.2	224.4	225.4
GB, kcal mole^{-1} (Ref.26)	214.9	215.4	216 4	217.3
$pK_{a(H_2O)}$	10.60	10.49	10.56	10.45

c) Aliphatic cyclic amines

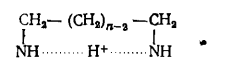
The basic strengths of several cyclic amines have been measured in the gaseous phase. Here, the basic strength increases with increase in the size of the ring, whereas in water it is practically constant[21] (Table 8).

Table 8. Basic strength of various saturated heterocyclic bases in the gaseous phase and in water[20,30].

Base			
PA, kcal mole^{-1}	231.5 230.1[21]	228.7	227
$pK_{a(H_2O)}$	11.22	11.27	11.29

d) Aliphatic diamines

Unexpected results were obtained in the study of the basic strength of alkylenediamines[30,32]. These substances were found to be very strong bases in the gaseous phase; they show a greater (by 10–20 kcal mole^{-1}) proton affinity than the corresponding monoamines. This is not observed in the liquid phase (Table 9). Proton transfer to the monoamine molecule in the gaseous phase is almost isentropic, that is $\Delta G^\circ = \Delta H^\circ$, whereas in the case of diamines there is a considerable decrease in entropy. This is related to the formation of an intramolecular hydrogen bond[32], which is assumed to be linear:



Studies of aqueous solutions of diamines have not detected hydrogen bonds of this type in monoprotonated diamines.

Table 9. Basic strength of mono- and diamines in the gaseous phase and in water[30,32].

Basic strength	*n* = 2	3	4	5	6	7
Monoamines $CH_3(CH_2)_nNH_2$						
PA, kcal mole^{-1}	222.3	222.8	223.1	223.2	—	—
$pK_{a(H_2O)}$	10.53	10.60	10.63	10.64	10.66	10.65
Diamines $NH_2(CH_2)_nNH_2$						
PA, kcal mole^{-1}	232;234.9	238.3;243.3	243.3;	241 3;	242.1;	—;
			—	243.3	—	243.2
$-\Delta S^\circ$, e.u.	12.7	20.6	—	20.0	—	20.0
$pK_{a(H_2O)}$	10.09	10.62	10.80	10.86	—	—

3. Basic Strength of Oxygen Bases in the Gaseous Phase

This question will not be dealt with in detail. The regular features here are in principle the same as in the case of amines. The basic strength of all oxygen compounds in the gaseous phase is greater than that of water; with increase in the number of carbon groups, their size, and their degree of branching, the basic strength increases in all cases[15,48,49].

1. Alcohols				
a) the effect of homology	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH
PA, kcal mole^{-1}	165	182, 180[51]	187, 186[51]	189
b) the effect of branching	CH_3OH	CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
PA, kcal mole^{-1}	182	187	193, 195[51]	198, 206[51]
2. Esters of carboxylic acids	$HCOOCH_3$	CH_3COOCH_3	$C_2H_5COOCH_3$	$CH_3COOC_2H_5$
PA, kcal mole^{-1}	188	202	205	205
3. Carboxylic acids	HCOOH	CH_3COOH	C_2H_5COOH	
PA, kcal mole^{-1}	175	188	190	
4. Oxo compounds	CH_2O	CH_3CHO	CH_3COCH_3	
PA, kcal mole^{-1}	168[51, 52]	183[49, 53]	202[48], 190[51]	

Table 10. Basic strength of various alkyl halides in the gaseous phase[50].

Basic strength	CH_3F	CH_3Cl	CH_3Br	CH_3I	C_2H_5F	C_2H_5Cl	C_2H_5Br	C_2H_5I
PA, kcal mole^{-1}	151	160	163	170	163	167	170	175

4. Basic Strength of Alkyl Halides and Alkenes in the Gaseous Phase

Alkyl halides are protonated according to the equation:

$$RX + H^+ \rightleftarrows (R{-}X{-}H)^+ .$$

In general, the readily understood order given in Table 10 [50]

is observed. An interesting feature is that the basic strength of alkyl halides in the gaseous phase is comparable with that of alkenes, benzene, and acetylene (Table 11).[51] This should be borne in mind for the study of the mechanism of gaseous reactions.

Table 11. Basic strength of various alkenes, benzene, and acetylene in the gaseous phase[51].

Basic strength	$CH_2=CH_2$	$CH_3CH=CH_2$	$C_2H_5CH=CH_2$	$(CH_3)_2C=CH_2$	C_6H_6	$CH\equiv CH$
PA, kcal mole^{-1}	160	179	183	195	183[a]	151

IV. RATIO OF THE BASIC STRENGTHS IN THE GASEOUS AND LIQUID PHASES

The study of the basic strength of organic substances in the gaseous phase and comparison with the basic strength in solutions lead to contradictory results. On the one hand, there is a marked lack of correspondence. between the values of the basic strength (ammonia–aniline, ammonia–pyrrole, ammonia–pyridine, trimethylamine–dimethylamine, etc.), and this undoubtedly requires a change in existing ideas regarding the factors determining basic strength in the liquid phase. On the other hand, there are cases where the structure of molecules influences the basic strength in the liquid and in the gaseous phases in qualitatively the same way (and sometimes quantitatively, with linearity of the free energies). Thus in some cases the liquid medium changes only the scale of the differences in the basic strength for a series of substances, leaving the order of the changes unaltered; in other cases, however, the actual order of the basic strength is altered. In these latter cases, the change from the gaseous phase, in which the basic strength of *isolated* molecules is measured, to the liquid phase, where the basic strength of molecules in a liquid environment, that is *solvated* molecules, is measured, has such a marked effect that the ratio of the basic strengths of the substances being compared is reversed. This question has been examined in detail by Taft and Arnett and coworkers[6,54,55], Aue and coworkers[23,26,56], and others; good reviews have been published by Arnett[55,57].

The basic strength in the liquid phase is determined by two factors: the "intrinsic" or "internal" basic strength, measured in the gaseous phase as the proton affinity (more accurately as $-\Delta G$ for the attachment of a proton), which is a property of the molecules themselves; and an external factor, the solvation factor, which is a property of the "molecule of the base + molecule of the medium" system[58]. The effect of the external factor may be stronger than the influence, to which we are accustomed, of the structure of the molecules of the base with their characteristic inductive and mesomeric effects; the effect of this factor often masks everything completely. Thus our explanations of the acid–base properties of substances in the liquid phase only by means of inductive effects (aliphatic amines, alcohols, esters), mesomerism (aniline and its derivatives, naphthylamines, etc.), and hybridisation (pyridine, quinoline, pyrimidine) are primitive and often simply incorrect.

It should be said that the theory of the gas-phase and liquid-phase basic strength of organic substances is still in the development stage. Many questions, not at all of secondary importance, are still disputed. These include the understanding of the essential features and role of the inductive effect of alkyl groups, polarisability in the stabilisation of ions, resonance and hyperconjugation effects, the effect of hybridisation, etc. The research groups of Aue and Kebarle on the one hand, and of Taft and Arnett on the other, have different views. The application of electrostatic concepts, widely used by Aue, is not favoured by other workers. Taft's efforts to break down all thermodynamic functions according to the additive contributions of the effects is not supported either, however. Some selections from the literature on this topic, which seem more correct to the present author, are discussed below.

The basic strength of organic substances is determined by the difference between the free energies of the neutral molecules and the corresponding protonated forms, in most cases onium ions. The main contribution is made by the stability of the ion MH^+. Ions are unstable in the gaseous phase. Once formed, they rapidly disappear by recombination with oppositely charged ions or on the walls. In the liquid phase, ions are stabilised by solvation, the energy of which may exceed the energy of formation of the ion from the molecule. The least stable in the gaseous phase are the simplest ions: H_3O^+, NH_4^+, NH_2^-, OH^- . . . . The replacement of a hydrogen atom in these ions by organic groups stabilises the ions by delocalisation of the ionic charge. Kebarle calls this "internal solvation" [7]. The greater the "capacity" of the organic group for delocalisation of the charge (in this sense, the higher its polarisability ‡), the greater the delocalisation, the more stable the ion, and, other conditions being equal, the higher the base strength.

Aniline in the gaseous phase is a stronger base than ammonia, so that the ammonium ion is unstable, and the anilinium ion is stabilised by delocalisation of the onium charge, possibly by an inductive–mesomeric mechanism. For an analogous reason, pyridine is a stronger base than ammonia, trimethylamine is a stronger base than dimethylamine, and the base strength (and acid strength) of aliphatic amines increases with increase in the number, size, and degree of branching of the hydrocarbon groups present[59–61]. This is confirmed by theoretical quantum-chemical calculations[62–65], although, as pointed out by Huheey[61], it would have been better if these calculations had not been carried out a posteriori.

Nevertheless, in the examination of the questions of base strength it is also necessary to take account of factors stabilising the neutral molecules of the base. Taft and coworkers[42] drew attention to the fact that comparison of the base strength of amines is justified only if they have equal numbers of carbon atoms and a similar skeleton. In this case aniline should be compared not with ammonia but with cyclohexylamine. The base strength of the latter is greater than that of aniline in the gaseous phase by

‡ Here and subsequently the concept of the polarisability of a group will be used only in the sense of the ability of this group, when attached to an ionic centre, to delocalise its charge.

9.6 kcal mole^{-1}. Taft[6] considers that the main contribution to this difference is made by the mesomeric stabilisation of the neutral aniline molecules (~ 5.5 kcal mole^{-1} according to Taft) §.

Similarly, according to Taft, pyridine should be compared not with ammonia but with, for example, N-methylpyrrolidine ($-\delta\Delta G^\circ$ in the gaseous phase 7.5 kcal mole^{-1}). In this case the role of the hybridisation effect is distinguished (the weighting of the *s*-orbital of the unshared pair of electrons of the nitrogen is greater for pyridine). Arnett points out that Aue[66] attributes too much importance to the hybridisation effect in the examination of the base strength of ethyleneimine (compared with dimethylamine). The question of the role of hybridisation has also been dealt with by Brauman and Blair[67].

Taft and, following him, Arnett probably overestimate the role of electronic effects in neutral molecules and underestimate their role in protonated ions (the polarisation effect according to Taft). In any case, our view that the mesomeric effect and the effect of hybridisation play a definite role in determining the base strength of organic substances is not refuted by the results of measurements in the gaseous phase. Those comparisons and conclusions unjustifiably based on incorrectly understood facts have been refuted.

The relationships change most significantly on going to the liquid phase. Appropriate thermodynamic studies were carried out by Arnett[55] by applying the Born cycle[68]:

$$\begin{array}{ccc} MH^+_{(gas)} & \xrightarrow{\Delta G^\circ_{ion(gas)}} & (M + H^+)_{(gas)} \\ \uparrow -\Delta G^\circ_{solv\ (MH^+)} & & \downarrow \Delta G^\circ_{solv\ (M+H^+)} \\ MH^+_{(liquid)} & \xrightarrow{\Delta G^\circ_{ion(liquid)}} & (M + H^+)_{(liquid)} \end{array} .$$

In this cycle, the ionisation of the cation MH^+ in the liquid phase takes place in two ways: the first is the ionic dissociation in the liquid phase, for which $\Delta G^\circ_{ion(liquid)} = -RT \ln K_{a(liquid)}$. The second is the desolvation of the cation (transfer to the gaseous phase, free energy of solvation $-\Delta G^\circ_{solv\,(MH^+)}$), dissociation in the gaseous phase ($\Delta G^\circ_{ion(gas)}$), followed by reverse transfer to the liquid phase ($\Delta G^\circ_{solv(M + H^+)}$).

The two routes naturally lead to the same free energy change, so that:

$$\Delta G^\circ_{ion(liquid)} = \Delta G^\circ_{ion(gas)} - \Delta G^\circ_{solv\,(MH^+)} + \Delta G^\circ_{solv\,(M+H^+)} .$$

If $\Delta G^\circ_{ion(liquid)}$ is known from the ionisation constant in the liquid phase, $\Delta G^\circ_{ion(gas)}$ from measurements in the gaseous phase, and $\Delta G^\circ_{solv(M + H^+)}$ from thermochemical measurements, it is possible to calculate $\Delta G^\circ_{solv(MH^+)}$. Similar cycles can be constructed for ΔH° and $T\Delta S^\circ$.

In fact, these calculations are carried out as relative calculations (usually relative to ammonia as reference standard). In this case the difficulties associated with the choice of standard states disappear, and, in addition, the terms relating to the proton are eliminated. In fact, this relative calculation is related not to the simple equilibrium $MH^+ \rightleftharpoons M + H^+$ but to the double equilibrium $MH^+ + NH_3 \rightleftharpoons M + NH_4^+$. Thus from the Born cycle:

$$\delta\Delta G^\circ_{ion(liquid)} = \delta\Delta G^\circ_{ion(gas)} - \delta\Delta G^\circ_{solv\,(MH^+)} + \delta\Delta G^\circ_{solv(M)} ,$$

where the latter δ denotes the relative change in the free energy (relative to the ionisation of NH_4^+).

The free energy of solvation of ions is very high. Its relative value may be only slightly less than the relative free energy of ionisation in the gaseous phase, but may be equal to it and even exceed it. If the difference in the free energies of solvation of the ions M_1H^+ and M_2H^+ being compared is less than the difference in the energies of ionisation in the gaseous phase, no anomalies are observed in the qualitative order of the change in base strength in the gaseous phase and in solution. If however the difference in the free energies of the solvation of the ions is greater than the difference in the free energies of ionisation in the gaseous phase, the above-mentioned lack of agreement will be observed between the base strength in the gaseous phase and the base strength in solution.

This is the case, for example, for aniline and ammonia. The protonation of aniline in the gaseous phase is energetically more favourable than the protonation of ammonia, by 7–8 kcal mole^{-1}. This means that the protonation constant of aniline is greater than that of ammonia by 5–6 orders of magnitude. When the ammonium ion is transferred to the aqueous phase, however, the large energy of solvation $-\Delta G_{solv(NH_4^+)} = 77.1$ kcal mole^{-1} is gained, and this is much greater than that for the transfer of the anilinium ion. As a result, the ammonium ion becomes energetically much more favourable than the anilinium ion in the aqueous phase. As a consequence, in the aqueous phase the protonation of aniline is less favourable by 6.5 kcal mole^{-1} than the protonation of ammonia (pK_a 9.27 and 4.58 respectively). Thus the fact that in the liquid phase aniline is weaker than ammonia is due to the less extensive solvation of the anilinium ion compared with the ammonium ion, and not to the basic properties of the unshared pair of electrons of the nitrogen atom in the aniline molecule.

A complete thermodynamic calculation has been carried out for many primary, secondary, and tertiary amines[26,54]. It has been found, for example, that in the case of trimethylamine, the protonation in the gaseous phase ($\delta\Delta G^\circ_{ion(gas)}$) is more favourable by 20.4 kcal mole^{-1} than in the case of ammonia, and the free energy of solvation of the trimethylammonium ion ($\delta\Delta G_{solv(MH^+)}$) is lower by 20.7 kcal mole^{-1}. In the gaseous phase, trimethylamine is a stronger base than ammonia, as a result of the inductive effect of the three methyl groups, but in the liquid phase this advantage is almost completely quenched by the less extensive solvation of the ion. Thus the basic strength of trimethylamine in the aqueous phase is only slightly greater than that of ammonia (by 0.8 kcal mole^{-1}).

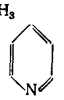
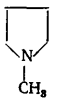
This quenching does not take place in the case of dimethylamine, which in water is a stronger base than trimethylamine. Here, the following results have been obtained for the MH^+ ion: $\delta\Delta G^\circ_{ion(gas)} = 15.8$ kcal mole^{-1}, $\delta\Delta G^\circ_{ion(liquid)} = 2.1$ kcal mole^{-1}, $\delta\Delta G^\circ_{solv(M)} = 0$, and

§ Here there may be one objection. Quantum-chemical calculation of the effective charges on the atoms in alkylammonium molecules[56] shows that the positive charge of the ion is distributed to the extent of more than 90% on the hydrogen atoms. It may therefore be doubted if it is justifiable to assign the observed differences to the resonance effect when comparing amines which satisfy only the requirement that the numbers of carbon atoms be equal and the skeleton similar, but for which the numbers of hydrogen atoms differ to such a great extent.

$\delta\Delta G^\circ_{solv(MH^+)}$ = 13.7 kcal mole^{-1}. In the gaseous phase, dimethylamine is weaker than trimethylamine $\delta\Delta G^\circ_{ion(gas)}$= 15.8 kcal mole^{-1} for $(CH_3)_2NH_2^+$ and 20.4 kcal mole^{-1} for $(CH_3)_3NH^+$, the difference in favour of trimethylamine being 4.6 kcal mole^{-1}). In aqueous solution, however, $\delta\Delta G^\circ_{ion(liquid)}$ = 0.8 kcal mole^{-1} for $(CH_3)_3NH^+$ and 2.1 kcal mole^{-1} for $(CH_3)_2NH_2^+$. The difference in favour of dimethylamine is 1.3 kcal mole^{-1}, in spite of the increased $+I$-effect in the case of trimethylamine from the introduction of the third methyl group. The difference in the hydration energies is greater.

Extensive data have been published[26] on the terms of the Born cycles for a number of bases. Of particular interest, for example, are the ratios[26] of the free energies of dissociation and solvation of the molecules and ions of pyridine, N-methylpyrrolidine, and piperidine, given in Table 12 (as before, the protonation of ammonia is taken as standard). Here, $-\Delta H^\circ_{solv(NH_4^+)}$ = 83.8 kcal mole^{-1}, $-\Delta G^\circ_{solv(NH_4^+)}$ = 77.1 kcal mole^{-1}¶.

Table 12. Born cycle data for pyridine, N-methylpyrrolidine, and piperidine[26] ($\delta\Delta G^\circ$, kcal mole^{-1}).

Compound	$\delta\Delta G^\circ_{ion(liq.)}$	$\delta\Delta G^\circ_{solv.(MH^+)}$	$\delta\Delta G^\circ_{ion(gas)}$	$\delta\Delta G^\circ_{solv.(M)}$
NH_3	0	0	0	0
	—5.49	26.9	18.9	1.99
	2.69	22.9	23.5	1.58
	1.65	27.9	26.4	2.71

In the gaseous phase, the protonation of pyridine is more favourable by 18.9 kcal mole^{-1} than the protonation of ammonia, but in aqueous solution, as a consequence of the loss of 26.9 kcal mole^{-1} for solvation, the protonation of pyridine is less favourable by 5.5 kcal mole^{-1} than that of ammonia. The relationships between pyridine and N-methylpyrrolidine are different. The protonation of the latter is more favourable both in the gaseous phase and in solution, by 7.5 kcal mole^{-1} in the gaseous phase and by 7.14 kcal mole^{-1} in solution. The effect of solvation is approximately the same in both cases (the difference is ~1.0 kcal mole^{-1}), and does not alter anything. This equality of the solvation effects apparently lies at the basis of Taft's rule[42], mentioned above.

¶ The change in the standard free energy for the transfer of 1 mole of NH_4^+ at a pressure of 1 atm from the gaseous phase to a hypothetical molal aqueous solution[69].

The free energy of solvation of an ion can be calculated approximately from the Born equation[68]:

$$-\Delta G^\circ_{solv}\ \frac{z^2e^2}{2r}\left(1-\frac{1}{D}\right).$$

According to this equation, the standard free energy of the transfer of a spherical ion of radius r, having a charge ze, from a vacuum to a medium with a dielectric constant D is proportional to the square of the charge and inversely proportional to the radius of the ion. The solvation energy decreases with increase in the radius of the ion. Moreover, on delocalisation of the charge, when $ze = \Sigma q_i$, the solvation energy decreases, since $\Sigma q_i^2 < z^2e^2$ (the sum of the squares is always less than the square of the sum). The purely electrostatic picture of solvation is naturally insufficient for an adequate description, but the relationships given are nevertheless useful for a qualitative examination of the part played by solvation. The greater the size of the ion and the more extensively delocalised the charge, the less extensive the solvation. It should be noted that the effect of decrease in solvation on delocalisation of the charge was first noted by Mason[70].

Thus the part played by the hydrocarbon groups attached to the atom which acts as protonation centre is appreciably different in the gaseous phase and in solution. In the gaseous phase, increase in the polarisability (in the sense of delocalisation capacity) of the groups — their number, size, degree of branching, etc. — stabilises the ions and hence makes the base stronger. In the liquid phase, increase in the volume and polarisability of the groups decreases solvation, destabilises the ion, and hence decreases the strength of the base.

In the liquid phase, it is also necessary to take account of the volume effect: increase in the volume of the ion in all cases requires the expenditure of work to create a cavity in the solvent; this work decreases the energy of solvation, particularly in highly associated solvents; the steric hindrance of solvation also decreases the solvation energy. On the other hand, it is also necessary to take account of the possible formation of hydrogen bonds or other complexes with the solvent, since this leads to a significant increase in the solvation energy. The effect of this factor is effectively illustrated by the decrease in the exothermic character of the hydration of primary, secondary, and tertiary substituted ammonium ions compared with the unsubstituted NH_4^+ ion.[55] For primary ammonium ions, $\delta\Delta H^\circ_{solv(MH^+)}$ has an average value of ~6.8 kcal mole^{-1}, for the secondary ions ~13 kcal mole^{-1}, and for the tertiary ions ~19 kcal mole^{-1}, that is there is a decrease of ~6 kcal mole^{-1} for each hydrogen bond lost. Within each type, however, the decrease in the solvation energy increases with the volume of the ion (±20% of the average value). Thus the effect of hydrogen bonds predominates in this case.

Aue and coworkers[26] consider that the number of hydrogen bonds formed by the alkylammonium ions with water does not play such an important role in determining the solvation energy. They attribute more importance to the strength of the hydrogen bonds, which decreases with decreased charge on the NH_X^+ group. Since the charge decreases with increased number of alkyl groups attached to nitrogen, the illusion is created that a part is played by the number of hydrogen bonds, which also decreases with increased number of alkyl groups. In Aue's opinion, hydrogen bonds produce only a slight change in the solvation energy; the main contribution to the solvation energy of ammonium ions is made by the hydrophobic solvation of the alkyl groups and the electrostatic effects in the spirit of the Born theory.

It can be seen that the question of the dependence of the solvation energy on the structure of a molecule is fairly complex. No rational approach has yet been developed for its complete interpretation or more particularly its theoretical calculation.

V. ACID STRENGTH IN THE GASEOUS PHASE

1. Acid Strength of Alcohols in the Gaseous Phase

The first qualitative results of the study of the acid strength of alcohols in the gaseous phase were obtained by Brauman and Blair in 1968.[46] They immediately attracted the attention of chemists, since they contradicted the accepted conclusions and ideas of theoretical organic chemistry. This was followed by the publication of a number of papers by different authors, confirming the results of Brauman and Blair. Qualitatively, they reduce to the following: the acid strengths of alcohols having a normal chain increase in the order[46,59]: $H_2O < CH_3OH < CH_3.CH_2OH < CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_2OH < CH_3CH_2.CH_2CH_2CH_2OH$, that is the acid strength in the gaseous phase increases with increase in the chain length. Branching of the group also leads to an increase in the acid strength, the effect being greater than the effect of the increase in its size: $CH_3OH < CH_3CH_2OH < (CH_3)_2.CHOH < (CH_3)_3COH < (CH_3)_3CCH_2OH$; $(CH_3)_3COH \geqslant n\text{-}C_5H_{11}OH$ †.

Increase in the formal $+I$-effect of the alkyl groups is accompanied by an increase in their electron-acceptor effect, that is the $-I$-effect. Similar relationships were observed for the acid strength of amines, as noted above.

Within the framework of the concept of the $+I$-effect, which is fixed for the alkyl groups, this sounds paradoxical. It can be shown, however, that we ourselves have created this paradox. The fact is that a constant $+I$-effect, characteristic of alkyl groups, is one of the dogmas characteristic of present-day work in organic chemistry. A dogma which has appeared from nowhere! Ingold, one of the founders of the electronic theory of organic chemistry, wrote in the early nineteen-thirties[71]: "It can be deduced from the premises stated above that the inductive effect of all alkyl groups *is zero* ... (They) will merely exert those polar effects which are impressed on them by the other polar groups ... The important property of alkyl groups is that they are more polarizable than hydrogen ... Since the majority of substituents commonly encountered are attractors of electrons, alkyl groups generally function as feebly electron-repelling groups: the possibility of the other type of behaviour can, however, be foreseen..."

Thus the direction of the inductive effect of alkyl groups depends on whether they are attached to an atom (or group) with a greater or lesser electronegativity than the alkyl groups. The first case leads to the relationships called the $+I$-effect, and the second to the relationships called the $-I$-effect.

This very perspicacious warning of Ingold was forgotten, and we teach students that alkyl groups exhibit a $+I$-effect. In fact, this is not the case. In proton attachment reactions, the principal role is played by the stabilisation of the cation formed, for example R_3N^+H or RO^+H_2. Here, the alkyl groups "deliver" electrons, since they are attached to an atom carrying a positive charge, that is an atom which is much more electronegative than the alkyl groups. Here, the larger the alkyl group, the greater its polarisability in the sense of "delocalisation capacity", the greater the $+I$-donor power and the greater the basic strength.

In the acidic dissociation of amines and alcohols, the principal role is played by the stabilisation of the resulting anion RNH^- or RO^-. Here, the alkyl groups "withdraw" electrons, since they are attached to an atom carrying a negative charge, that is an atom which is less electronegative than the alkyl groups. In this case, the larger the alkyl, the stronger its $-I$-effect, leading to greater acidity. Thus the t-butyl and neopentyl groups are both the strongest donors and the strongest acceptors among the alkyl groups, since they have the greatest ability, among alkyl groups, to delocalise any charge (Brauman and Blair[59-61]). Later, Arnett and coworkers[37] supported this view. The acid strength of alcohols in the vapour phase was also examined theoretically by MINDO and CNDO/2 methods and calculated *ab initio*. The results confirmed these suggestions. Reversal of the order of acid strength of the alcohols is observed on going to the liquid phase. The factors responsible are the same as in the case of the basic strength of amines. The smaller the anion, the stronger the effect of solvation. The order is reversed, not because of the $+I$-effect, which is not present in this case, but because of the solvation effect.

2. Acid Strength of Carboxylic Acids in the Gaseous Phase

The acid strength of carboxylic acids in the gaseous phase is expressed as the free energy change in the dissociation:

$$RCOOH \rightleftarrows RCOO^- + H^+ ,$$

When a standard acid AH is used, relative measurements are made for the reaction:

$$RCOOH + A^- \rightleftarrows RCOO^- + AH ,$$

In these reactions, the entropy change is small and does not exceed 1–2 e.u., so that it is usually assumed that $\Delta G^\circ = \Delta H^\circ$, and the acid strength is measured by the proton affinity of the anion, that is the enthalpy of the reaction

$$A^- + H^+ \rightarrow AH,$$

taken with the opposite sign ($-\Delta H^\circ$).

It is possible to write:

$$\Delta H^0 = D\,(A{-}H) + IP\,(H) - EA\,(A),$$

where $D(A-H)$ is the energy of rupture of the bond, O–H, $IP(H)$ the ionisation potential of atomic hydrogen, and $EA(A)$ the electron affinity of the radical $RCO\dot{O}$. Since $IP(H)$ is a constant equal to 313.6 kcal mole^{-1}, a measure of the acid strength is usually obtained by calculating the quantity

$$\delta\Delta H^0 = D\,(A{-}H) - EA\,(A), \text{ that is } \delta\Delta H^0 = \Delta H^0 - IP\,(H) = \Delta H^0 - 313{,}6$$

(kcal mole^{-1}). For water, $D(A-H) - EA(A) = D(HO-H) - EA(OH^\cdot) = 77$ kcal mole^{-1}. In the gaseous phase, water is a very weak acid. All other oxygen acids are stronger,

† McIver's group[37] carried out quantitative measurements of the acid strength of various alcohols in the gaseous phase relative to methanol The following values were obtained for $-\delta\Delta G_{ion(ROH)}$ in kcal mole^{-1} (at 298 K; an increase in the numerical value indicates an increase in the acid strength): CH_3OH 0, C_2H_5OH 2.9, iso-C_3H_7OH 4.8, t-C_4H_9OH 5.6, neo-$C_5H_{11}OH$ 6.9. These data confirm the qualitative conclusions of Brauman and Blair.

that is their $\delta\Delta H^\circ$ values are less than 77 kcal mole^{-1}, and the smaller the numerical value of $\delta\Delta H^\circ$, the stronger the acid.

In the homologous series of carboxylic acids, the value of $\delta\Delta H^\circ$ for ionisation decreases with increase in the number of carbon atoms (Table 13 [24]). Thus butyric acid is stronger than propionic acid, and propionic acid is stronger than acetic acid; the order is reversed compared with the acid strength in water or other liquid media. Formic acid is the strongest acid in this series, however. To enable the reader to estimate the numerical values of the strength of acids in the gaseous phase ($\delta\Delta F^\circ$), the gaseous acid strength of the hydrogen halides is given (Table 14).

Table 13. Acid strength of various carboxylic acids in the gaseous phase and in water[24].

Acid strength	CH_3COOH	C_2H_5COOH	C_3H_7COOH	HCOOH
$\delta\Delta H^0$, kcal mole^{-1}	31.8	30.6	29.7	28.6
pK_a (H_2O)	4.76	4.87	4.82	3.75

Table 14. Acid strength of hydrogen halides in the gaseous phase and in water[24,74].

Acid strength	HF	HCl	HBr	HI
$\delta\Delta H^0$, kcal mole^{-1}	56.3	20.0	10.0	0.7
pK_a (H_2O)	+3.2	−7	−9	−11

The study of the gas-phase acid strength of halogen-substituted carboxylic acids gave unexpected results. They are of course stronger than the unsubstituted acids (Table 15).

Table 15. Acid strength of chloroacetic acids in the gaseous phase and in water[24].

Acid strength	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$
$\delta\Delta H^0$, kcal mole^{-1}	31.8	19.0	12.0
pK_a (H_2O)	4.76	2.86	1.25

The order of the halogens is here reversed, however, compared with the liquid phase (Table 16). Bromoacetic acid in the gaseous phase (that is in itself) is stronger than chloroacetic acid, and the latter in turn is stronger than fluoroacetic acid; the concept of the *-I*-effect does not apply. The electronegativities of the halogens decrease in the order F > Cl > Br. This means that there are other factors in addition to the *-I*-effect (which is observed in the comparison with the unsubstituted acid). In fact, in the XCH_2COO^- anion, bromine is apparently more readily polarised, and its polarisation by the anionic charge stabilises the anion (the negative charge is delocalised). In an aqueous or in general liquid medium, on the other hand, in least polarisable fluorine-containing anion, in which the negative charge is concentrated in a small volume, is most effectively stabilised by the liquid medium; in the liquid phase, fluoroacetic acid is stronger than the others.

Table 16. Acid strength of various halogenoacetic acids in the gaseous phase and in water[75].

Acid strength	FCH_2COOH	$ClCH_2COOH$	$BrCH_2COOH$
$\delta\Delta H^0$, kcal mole^{-1}	21.0	19.0	17.9
pK_a (H_2O)	2.57	2.86	2.90

If however the carboxylic acid molecule contains substituents which each exhibit inductive and mesomeric effects, but which produce only slight changes in the total "delocalisation capacity" of the acid residue, the usual influence of electronic effects on the acid strength are observed satisfactorily in this series of derivatives. This is the case for the benzoic acid derivatives XC_6H_4COOH (X = NH_2, CH_3O, HO, CH_3, Cl, F, CN, NO_2). In this series, satisfactory correlations were obtained between ΔG° for dissociation in the gaseous phase (and pK_a in liquid phases) and the constants σ of Brown and Taft[31].

3. Acid Strength of Phenols in the Gaseous Phase

Here, reference may be made to the literature[35,75].

Table 17. Acid strength of thiols in the gaseous phase and in water[76].

Acidity	H_2S	t-C_4H_9SH	iso-C_3H_7SH	n-C_3H_7SH	C_2H_5SH	CH_3SH
$\delta\Delta H^0$, kcal mole^{-1}	37.5	39.4	40.3	41.1	41.7	43.2
pK_a (H_2O)	7.02	11.05	10 89	10.78	10.61	10.33

4. Acid Strength of Thiols in the Gaseous Phase[76]

Here, very interesting relationships are observed (Table 17). Hydrogen sulphide is a stronger acid than thiols both in the gaseous phase and in aqueous solution. In the gaseous phase, however, the strongest acid among the thiols is t-butyl mercaptan, which is the weakest acid in water. On the other hand, methanethiol, which is the

weakest acid in the gaseous phase, is a stronger acid than the other thiols in water. These relationships show a greater resemblance to those for the carboxylic acids than to those for the alochols (where water is weaker than all alcohols). The explanation for these phenomena is apparently similar to the explanation of the influence of alkyl groups on the strength of carboxylic acids (see below).

5. CH Acid Strength of Hydrocarbons and Their Derivatives

Carbon atoms in the hybridisation states sp^2 or sp have a greater electronegativity than in the state sp^3. Thus the bond $C_{(sp^3)} - C_{(sp^2)}$ should have a dipole moment directed from the sp^3- to the sp^2-hybridised carbon atom:

$$C_{(sp^3)} \longrightarrow C_{(sp^2)} .$$

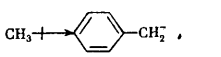
Thus alkyl groups should exhibit the familiar donor $+I$-effect. In this connection, the acid strengths of various unsaturated and aromatic hydrocarbons were studied in the gaseous phase[67]. The following series were obtained (some of the quantitative data are given in Ref. 36):

$$C_6H_5OH > C_6H_5CH_3 > CH_3OH > n\text{-}(CH_3C_6H_4CH_3 > H_2O;$$
$$CH \equiv CH > n\text{-}C_4H_9C \equiv CH > CH_3C \equiv CH > H_2O.$$

Here everything is remarkable!

1. Toluene is found to be a stronger acid than water. This indicates that the benzyl anion $C_6H_5CH_2^-$ is intrinsically more stable than OH^-. This is understandable, since the OH^- anion in the gaseous phase, that is when there is no solvation, is very unstable.

2. The fact that *p*-xylene is less acidic than toluene indicates that the methyl group has a destabilising action in the anion, since here the methyl "delivers" electrons ($+I$-effect):



3. Similarly, aklylacetylenes are less acidic than acetylene itself. A destabilising effect is present:

$$R \longrightarrow C \equiv O^- .$$

4. It is much more difficult to explain why t-butylacetylene is nevertheless a stronger acid than methylacetylene (by 3.4 kcal mole^{-1}). For this case, an apparently justified explanation has been put forward. In the general case, the stability of an anion is influenced by the dipole

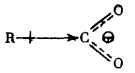
$$C_{(sp^3)} \longrightarrow C_{(sp)}$$

but in the butyl derivative the charge on the positive end of the dipole is assigned to the butyl group, which has a greater volume and polarisability. This decreases slightly the destabilising action of the alkyl group compared with the methyl group.

The question of the strength of carboxylic acids can now be considered:

$$HCOOH > C_3H_7COOH > C_2H_5COOH > CH_3COOH .$$

Here it is necessary to consider the system



containing the bond

$$C_{(sp^3)} \longrightarrow C_{(sp^2)} .$$

The action of an alkyl group produces a dipole, which is directed from the carbon atom of the alkyl group to the carbon atom of the carboxylate anion and destabilises the anion‡. This destabilisation, which is greatest for the methyl group, decreases slightly with increase in the size of the alkyl group, as a consequence of the delocalisation of the charge at the positive end of the dipole.

In an aqueous medium, however, the stability of the anion decreases with increase in its volume: $HCOOH^- > CH_3COO^- > C_2H_5COO^- > C_3H_7COO^-$, since there is a decrease in solvation, and the familar order of acid strengths is obtained:

$$HCOOH^- > CH_3COOH^- > C_2H_5COOH^- > C_3H_7COOH^- \ldots$$

This explanation naturally requires verification, but in any case this order cannot be attributed to the $+I$-effect of the alkyl groups (as is done in the most recent and best textbooks of organic chemistry).

6. Acid Strength of Ketones in the Gaseous Phase

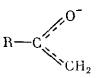
Recently, Brauman and coworkers[77] determined the acid strength of various ketones in the gaseous phase. The following order of acid strength was obtained:

$$C_6H_5COCH_3 > (CH_3)_3CCOCH_3 > CH_3COCH_3.$$

This differs from the order of acid strength in the liquid phase[78]:

$$C_6H_5COCH_3 > CH_3COOH_3 > (CH_3)_3CCOCH_3.$$

Here, the factors operating are apparently the same as in the case of carboxylic acids. In the anion



compared with the anion of acetaldehyde (R =H), the alkyl groups have a destabilising action (the dipole is directed to the anionic centre).

$$R \longrightarrow C_{(sp^2)}$$

This destabilising action is least for R = t-Bu, and greatest for R = CH_3. In the liquid phase, for reasons which are readily understood, acetone and methyl t-butyl ketone change places.

VI. SUMMARY

The intrinsic acid–base properties of molecules are observed only in the gaseous phase. In a liquid medium, these properties are distorted; they are deformed by the very strong interaction with the medium. In the examination of acid–base properties (and chemical properties in general) in the liquid phase, that is properties which necessarily belong to the system "molecule of the reactant plus surrounding molecules of the medium", these properties have been assigned only to the molecule of the

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‡ It should be noted that the effect of the dipole $C_{sp^3} - C_{sp^2}$ or $C_{sp^3} - C_{sp}$ is also observed in other cases. Thus prōp-2-ynylamine in the gaseous phase is a weaker base than propylamine by 6.3 kcal mole^{-1}; diprop-2-ynylamine is weaker than dipropylamine by 10.5 kcal mole^{-1}, and triprop-2-ynylamine is weaker than tripropylamine by 13.7 kcal mole^{-1} [6]. This results from the fact that in the corresponding cations $(CH \equiv C\text{-}CH_2)_nNH_{4-n}^+$ the dipole $C_{sp^3} \rightarrow C_{sp}$ destabilises the cation. Taft calls these hybridisation–inductive effects.

reactant, and very beautiful but incorrect explanations have been constructed from the non-existent consequences of the action of inductive and mesomeric effects. These ideas have been re-examined in recent years.

The present review has dealt with only proton transfer reactions. The same situation is observed in reactions of other types. Extremely interesting results have been obtained by Kebarle's group[7] in the study of ionic clusters in the gaseous phase. These products of the attachment of neutral molecules to ions provide models of short-range order on solvation ("supermolecule" formation). Reactions involving addition to multiple bonds, nucleophilic substitution at a saturated carbon atom, and other reactions have also been studied in the gaseous phase. In these fields it has been found that the role of intramolecular effects in neutral molecules has been exaggerated and frequently distorted, and the problems of the stability of ions in relation to the influence of solvation have been insufficiently analysed. It is now time for a painstaking re-examination and correction of all the errors made in theoretical organic chemistry in the last 40 years. We are standing on the threshold of great events in the theory of heterolytic reactions in organic chemistry, which will be realised in the near future.

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§ According to a personal communication from McIver, the results of this work will be revised; see Ref. 6.

¶ These data were subsequently refined; see R. W. Taft and M. Taagepera, Abstracts of the 167th ACS National Meeting, Los Angeles, April, 1974.

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The Isomerisation of Unstable Organoelemental Radicals in Liquid-phase Reactions

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The studies carried out in recent years on the rearrangement of radicals involving the migration of Cl and Br atoms as well as the R_3Si, R_3Ge, RC = O, $RC\overset{O}{\underset{O}{<}}$, and RS groups in liquid-phase reactions are examined. Chemical and physicochemical data (obtained by EPR, stereochemical, tracer atom, etc. methods), supporting the idea of the intermediate formation of bridging radicals in 1,2- and 1,3-migrations of atoms and groups, are presented. The unusual rearrangements of aromatic perfluoro-radicals are discussed.
The bibliography includes 113 references.

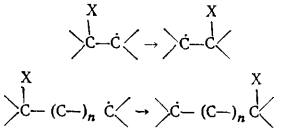
CONTENTS

I. Introduction 828
II. Rearrangements of radicals with migration of chlorine, bromine, and fluorine atoms 829
III. Rearrangements of radicals with migration of organoelemental groups 833

I. INTRODUCTION

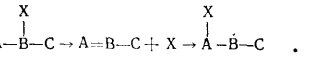
Studies on the rearrangements of organic radicals in the liquid phase constitute a rapidly developing field of modern radical chemistry[1-8]. The wide variety of the known types of rearrangements of radicals is due to the differences in the nature of the migrating groups, the variable nature of the atoms from which the migrating group is split off, the nature of the radical centre, and the length of the chain separating the radical centre from the migrating atom or group.

This review deals with true intramolecular rearrangements associated with the migration of atoms or groups via the mechanisms



It includes the rearrangements of radicals involving the migration of Cl, Br, and F atoms and of the R_3Si, R_3Ge, $RC\overset{O}{\underset{O}{<}}$, RCO, and RS groups; the literature on these rearrangements up to 1978 inclusive is considered. Despite all the differences between them, the above types of rearrangements have the following common features: the structure of the hydrocarbon skeleton of the radical remains unchanged in the rearrangement; heteroatoms (halogens) or groups incorporating heteroatoms (R_3Si, R_3Ge, RCO, RCOO, or RS) migrate; the migrating atoms or groups contain lone electron pairs, π-bonds, or unoccupied *d* orbitals.

All the known rearrangements of short-lived radicals can apparently be divided into two types: (1) rearrangements of radicals involving the migration of a hydrogen atom; (2) rearrangements involving the migration of atoms and groups containing lone electron pairs, π-bonds, and vacant *d* orbitals. These two types of rearrangements differ in their characteristics. For example, the 1,2-migration of hydrogen in radicals is virtually unknown; on the other hand, 1,2-migration and to a lesser extent 1,3-migration of atoms and groups are characteristic of all the rearrangements considered in the present review. An important problem for the understanding of 1,2-rearrangements involves criteria which make it possible to distinguish an intramolecular rearrangement from the formation of rearranged radicals via an elimination–addition mechanism, which can be formally represented schematically as follows:



In certain cases it is possible to distinguish these two types of reaction. The detection of the eliminated migrating group with the aid of a suitable trapping agent is sometimes used as proof that the reaction proceeds via an elimination–addition mechanism. It is noteworthy that this method does not provide an unambiguous answer, since the migrating group can be split off simultaneously with an intramolecular rearrangement.

The formation of intermediate three-membered bridged intermediate radicals or a bridged transition state is postulated for all the rearrangements involving 1,2-migration of atoms enumerated above. Indeed, it has been shown by EPR in instances where it was possible to obtain a resolved spectrum that the presence of chlorine and silyl, germyl, and certain other groups in the β-position with respect to the radical centre has a marked influence on the conformation of the radical. Thus a detailed study of the spectroscopic parameters of β-chloroalkyl radicals and their temperature variation showed[8] that in the most stable conformation of this radical the chlorine atom is located in the "eclipsed" position relative to the *p* orbital of the radical centre, which is favourable for the interaction between them.

The formation of bridged radicals can be to some extent detected by chemical methods. Thus anchimeric cooperation with the selective elimination of hydrogen from the β-position with respect to the atom or group which is capable of forming a bridged radical is observed in some reactions. A characteristic feature of the intermediate formation of a bridged radical is also the retention of optical activity in reactions involving a rearrangement of radicals.

Most of the known rearrangements of radicals have been investigated by methods of preparative organic chemistry. It can now be assumed that the information obtained by these methods about the radical-chain mechanisms of the rearrangements, the structures of the rearranged and non-rearranged radicals, and the intramolecular nature of the reaction has been confirmed in

many instances by various physicochemical methods (EPR, stereochemistry, tracer atoms, etc.).

II. REARRANGEMENTS OF RADICALS WITH MIGRATION OF CHLORINE, BROMINE, AND FLUORINE ATOMS

1. 1,2-Migration of Chlorine

Nesmeyanov et al.[9] first demonstrated reliably, in the case of the rearrangement of polychloroalkyl radicals I to radicals II with 1,2-migration of chlorine (1,2-Cl), the possibility of the liquid-phase isomerisation of unstable aliphatic radicals:

$$\underset{\text{(I)}}{XCCl_2\dot{C}YCH_2Z} \rightarrow \underset{\text{(II)}}{X\dot{C}ClCYClCH_2Z} \ ;$$

X=H, F, Cl, or CH_3; Y=H, Cl, Br, or CH_3; Z=Br, CCl_3, or SR.

The possibility of such a rearrangement in the above investigation has been questioned[10]. Radicals of type (I) have been generated by the addition of the radicals Ż to polychloropropenes $CH_2 = CYCCl_2X$. For the reaction of 3,3,3-trichloropropene with HBr initiated by benzoyl peroxide, the following scheme has been put forward:

$$HBr + C_6\dot{H}_5 \rightarrow C_6H_6 + \dot{B}r \ :$$
$$\dot{B}r + CH_2{=}CHCCl_3 \rightarrow BrCH_2\dot{C}HCCl_3 \ :$$
$$BrCH_2\dot{C}HCCl_3 \xrightarrow{\text{rearrangement}} BrCH_2CHCl\dot{C}Cl_2 \ :$$
$$BrCH_2CHCl\dot{C}Cl_2 + HBr \rightarrow BrCH_2CHClCCl_2H + \dot{B}r \text{ etc.} \qquad (1)$$

Data on this rearrangement (literature up to 1964) have already been surveyed[4] (see also Wilt[2] and Walling[5]). In recent years rearrangements of this type have been investigated vigorously, but comparatively few new examples have been described. In particular, a study has been made of the rearrangement of primary radicals (III) to radicals (IV):

$$\underset{\text{(III)}}{CCl_3\dot{C}H_2} \rightarrow \underset{\text{IV}}{\dot{C}Cl_2CH_2Cl} \ .$$

This rearrangement was investigated by methods of preparative chemistry[11], EPR,[12,13] and the spin trapping technique[14,15]. Other examples of rearrangements of this type have been found[16-18] in the decomposition of acetyl peroxide in polychloroethanes and polychloropropanes containing the CCl_3, $CHCl_2$, or CCl_2 groups; among other products, there are compounds whose formation is treated as a 1,2-Cl rearrangement via mechanisms analogous to mechanism (1).

The rearrangement of β-monochloroalkyl radicals with 1,2-migration of chlorine has been described in recent years for radicals obtained by the abstraction of hydrogen from $(CH_3)_3CCl$ by t-butoxy-radicals[19]:

$$(CH_3)_3CCl \xrightarrow{RO\cdot} (CH_3)_2CCl\dot{C}H_2 \rightarrow (CH_3)_2\dot{C}CH_2Cl \xrightarrow{ROBr} (CH_3)_2CBrCH_2Cl \ .$$

Analogous rearrangements have been observed with the aid of EPR at low temperatures. The rearranged radicals have been identified by this method in reactions involving the abstraction of bromine from $(CH_3)_2CClCH_2Br$ and $CH_3CBrHC(CH_3)_2Cl$ by $(C_2H_5)_3Si$ radicals[12] and the abstraction of hydrogen from $(CH_3)_3CCl$.[12] The rearranged radicals, obtained by γ-irradiation from $(CD_3)_3CCl$, have been identified by EPR.[20]

The rearrangement of radicals with 1,2-migration of chlorine from C to Si in the gas phase[21] and from S to C in the liquid phase[22] has been described.

The study of the 1,2-Cl rearrangement on interaction of polyhalogenohydrocarbons with diazomethane has been developed to some extent[23]. The reactions of polyhalogeno-derivatives with diazomethane had been described earlier[24]:

$$CCl_4 + CH_2N_2 \xrightarrow{h\nu} (ClCH_2)_4C \ ;$$
$$XCCl_3 + CH_2N_2 \xrightarrow{h\nu} XCH_2C(CH_2Cl)_3 \ ;$$
X=H, Br, or CH_3CO_2 .

It has been suggested[24] that the reaction involves a series of consecutive stages in which methylene adds to the radical centre with subsequent 1,2-Cl migration. New examples of reactions of this type have been studied in recent years[23] and it has been shown that, depending on the reactant ratio and temperature, it is possible to isolate from the reaction mixture products obtained by the stabilisation of intermediate rearranged radicals formed by an exchange reaction with the initial polyhalogeno-derivative. For example, the reaction of diazomethane with $BrCCl_3$ led to the isolation of $BrCCl_2CH_2Cl$, $BrCCl.(CH_2Cl)_2$, $BrC(CH_2Cl)_3$, and $BrCH_2C(CH_2Cl)_3$. Analogous compounds were obtained in the reaction of diazomethane with $BrCCl_2CH_2Cl$, $BrCCl_2CH_3$, or $BrCCl_2H$.[23] A possible mechanism of this reaction has been discussed in detail in a review[2].

There are no data on the kinetics of the elementary stage of the 1,2-Cl rearrangement. The overall kinetics of reactions of this type, initiated by ultraviolet irradiation or benzoyl peroxide at 60°C, have been investigated in relation to the homolytic isomerisation of polyhalogenopropenes via the mechanism[25]

$$XCCl_2CBr{=}CH_2 \xrightarrow{h\nu} XCCl{=}CClCH_2Br \ (X{=}Cl, CH_3, \text{or F}) \ . \qquad (2)$$

It was established that the reaction is fastest in the case of 2-bromo-3,3,3-trichloropropene ($k = 2.2 \times 10^{-4}$ s^{-1}), which is followed by 2-bromo-3,3-dichlorobutene ($k = 1.5 \times 10^{-5}$ s^{-1}), the isomerisation of 2-bromo-3,3-dichloro-3-fluoropropene being slowest ($k = 5 \times 10^{-6}$ s^{-1}), It has been shown that the chain propagating species is the bromine atom. The quantum yield in the photochemical initiation of the isomerisation of 2-bromo-3,3,3-trichloropropene has been determined as 980 ± 30. The data obtained confirmed the mechanism of this rearrangement proposed by Nesmeyanov et al.[26] and made it possible to specify the chain initiation and termination stages. Presumably, the above series, in terms of decreasing rates of isomerisation of polyhalogenopropenes, corresponds to the series based on decreasing stabilities of the rearranged radicals:

$$Cl_2\dot{C}CBrClCH_2Br > CH_3\dot{C}ClCBrClCH_2Br > F\dot{C}ClCBrClCH_2Br \ .$$

It has been noted in the literature that most of the known rearrangements lead to the formation of more stable radicals from less stable ones. However, a number of instances are known in which the non-rearranged and rearranged radicals do not differ in stability; rearrangements have also been encountered in which more stable and relatively unreactive radicals rearranged to more reactive radicals with a lower stability. Certain examples of 1,2-Cl rearrangements of secondary chloroalkyl radicals to yield less stable primary radicals have been published[4]. However, comparatively few examples of such rearrangements are known and they give a low yield of the rearranged products. The calculation of the total electronic energies of two pairs of radicals is therefore of interest: $ClCH_2\dot{C}HCCl_3$ (V) and $ClCH_2CHCl\dot{C}Cl_2$ (VI); $ClCH_2\dot{C}ClCHCl_2$ (VII) and $ClCH_2CCl_2\dot{C}HCl$ (VIII). Radicals (VI) and (VIII) should be formed in the 1,2-Cl

rearrangement of radicals (V) and (VII) respectively. It had been shown earlier that radicals of type (V) do indeed rearrange to radicals (VI); under the same conditions, radical (VII) does not rearrange[4]. Calculation[27] showed that the relative stabilities of the radicals depend on their conformations and that, among the radicals enumerated above, radical (VI) is the most stable; the rearrangement of (V) to (VI) should be accompanied by an energy gain. The energies of radicals (VII) and (VIII) in the ground state differ little, but the rearrangement of radical (VII) to (VIII) nevertheless requires an expenditure of energy:

$$E\,(ClCH_2\dot{C}HCl_2) - 0.85\ eV = E\,(ClCH_2CHCl\dot{C}Cl_2)\ ;$$
$$E\,(ClCH_2\dot{C}ClCHCl_2) + 0.06\ eV = E\,(ClCH_2CCl_2\dot{C}HCl)\ .$$

The absence of the rearrangement of radical (VII) to radical (VIII) with 1,2-migration of chlorine is thus apparently really associated with the unfavourable ratio of the stabilities of the above radicals, as had been suggested previously[4].

The rearrangement of radicals with 1,2-migration of chlorine has been observed also in the polymerisation of polyhalogenopropenes. It has been established[28,29] that the radical polymerisation of 3,3,3-trichloropropene and 3,3-dichloro-3-fluoropropene leads to polymers which contain mainly the rearranged $CH_2CClHCCl_2$ and $CH_2CH.ClCClF$ units respectively according to ^1H and ^{19}F NMR and ^{35}Cl NQR data.

Rearrangements with 1,5- and 1,6-migration of chlorine in chloroalkyl radicals proceed with difficulty if they are possible at all. Indirect data supporting the possibility of 1,5-Cl and 1,6-Cl rearrangements have been published[30-32].

The application of the EPR method and the spin trapping technique in the study of rearrangements with 1,2-migration of chlorine. Significant progress in identifying rearranged and non-rearranged radicals, formed in many reactions and in demonstrating the intramolecular nature of the rearrangements has been achieved in recent years with the aid of the EPR method, including the use of spin-trapping agents.

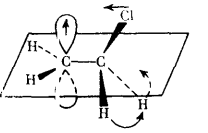
β-Chloroalkyl radicals. A number of workers have shown that the chlorine atom in the β-position with respect to the radical centre has a strong influence on the conformation of the radical[3,12,13,20,33,34], as had been observed earlier for certain other β-substituted alkyl radicals[35]. The EPR spectrum of the radicals obtained from t-butyl chloride under the influence of ^{60}Co γ-rays at 77 K exhibits a very large splitting between the components due to the hyperfine interaction (HFI) with the halogen atom[20].

The following HFI constants have been found for the EPR spectrum of $\dot{C}H_2CH_2Cl$: $a_\alpha(H) = 21.5$ G, $a_\beta(H) = 11.5$ G, and $a_\beta(Cl) = 17.4$ G at $-60°C$;[12] $a_\alpha(H) = 21.75$ G, $a_\beta(H) = 10.20$ G, $a_\beta(^{35}Cl) = 18.78$ G, and $a_\beta(^{37}Cl) = 15.65$ G at $-125°C$;[3] $g = 2.60199$. These data correspond to an asymmetric bridged structure (A) in which the chlorine atom eclipses the orbital of the odd electron, which requires a definite deviation from the regular tetrahedral geometry at the β-carbon atom[36]:



(A)

The EPR spectra have been investigated in greatest detail for a series of β-chloroalkyl radicals[3,13,33,37]. A detailed study of the spectral parameters—the g-factor, the hyperfine interaction constants for the β-protons and β-chlorine atoms, their temperature dependence, and the width of the lines in the spectrum—led to the conclusion[3] that the most stable conformation of the β-chloroethyl radical is of the type illustrated below†:



In this "eclipsed" conformation the chlorine atom is located at the optimum position for interaction with the radical centre. In conformity with Kochi's cautious formulation[3], the EPR data suggest that the structure of the β-chloroalkyl radicals can be regarded as the bridged type in a broad sense of the term. Radicals with chlorine in a more remote position relative to the radical centre cannot exist in the analogous conformation and do not isomerise with 1,3-, 1,4-, or 1,5-migration of chlorine. Bearing this fact in mind as well as the observed conformation of the β-chloroalkyl radicals, one can regard it as established that the 1,2-migration of chlorine in monochloroalkyl radicals has an intramolecular mechanism.

Table 1. EPR study of the rearrangement of radicals with 1,2-migration of chlorine.

Initial compound	Attacking radical	t, °C	Non-rearranged radicals (unidentified)	Rearranged radicals (identified)	Refs.
CH_3CCl_3	$CF_3O^\cdot$	−140	$\dot{C}H_2CCl_3$	$ClCH_2\dot{C}Cl_2$	13
$BrCH_2CCl_3$	$Et_3\dot{S}i$	−140	$\dot{C}H_2CCl_3$	$ClCH_2\dot{C}Cl_2$	13
ICH_2CCl_3	$n\text{-}Bu_3\dot{S}i$	−120	$\dot{C}H_2CCl_3$	$ClCH_2\dot{C}Cl_2$	12
$(CH_3)_2CClCH_2Br$	$Et_3\dot{S}i$	−110 −130	$(CH_3)_2CCl\dot{C}H_2$	$(CH_3)_2\dot{C}CH_2Cl$	12, 33
$(CH_3)_2CClCHBrCH_3$	$Et_3\dot{S}i$	−60	$(CH_3)_2CCl\dot{C}HCH_3$	$(CH_3)_2\dot{C}CHClCH_3$	12, 33
$(CH_3)_3CCl$	t-BuO·	−200	$(CH_3)_2CCl\dot{C}H_2$	$(CH_3)_2\dot{C}CH_2Cl$	12, 33
$(CD_3)_3CCl$	($\gamma^{60}Co$)	−196	$(CD_3)_2CCl\dot{C}D_2$	$(CD_3)_2\dot{C}CD_2Cl$	20

Rearranged radicals were identified by EPR in the liquid phase at low temperatures in the reactions presented in Table 1; non-rearranged radicals were not detected. Despite the incompleteness of the information obtained, these data are extremely important. They confirm the radical mechanism of the rearrangements, the high rate of 1,2-migration of chlorine in the radicals, and the greater stability of the rearranged radicals compared with the non-rearranged radicals.

gem-Polychloroalkyl radicals. For the purpose of the identification of both rearranged and non-rearranged radicals, the EPR method combined with the spin-trapping technique proved to be fruitful (Table 2).[34] The method has definite advantages for the solution of this problem. The spin-adducts (nitroxy-radicals) formed

† The arrows indicate the direction of the shifts of atoms in the transition state.

Table 2. EPR study of the rearrangements with 1,2-migration of chlorine using spin trapping agents.

No.	Initial compound	Attacking radical	t, °C	Non-rearranged radical (NR)	Trapping agent for NR	Rearranged radical (RR)	Trapping agent for RR	Refs.
1	$BrCH_2CCl_3$	$Et_3\dot{S}i$	−60	$\dot{C}H_2CCl_3$	MNP	$ClCH_2\dot{C}Cl_2$	Nitrosodurene	41
2	$ClCH_2CCl_3$	$P\dot{h}$	25	$Cl\dot{C}HCCl_3$	MNP	$Cl_2CH\dot{C}Cl_2$	MNP	14
3	$CH_2=CHCCl_3$	$(CH_3)_3C\dot{O}$	25	$(CH_3)_3COCH_2\dot{C}HCCl_3$	MNB	$(CH_3)_3COCH_2CHCl\dot{C}Cl_2$	MNP	43
4	$CH_2=CHCCl_3$	$\dot{C}Cl_3$	25	$CCl_3CH_2\dot{C}HCCl_3$	MNB	$CCl_3CH_2CHCl\dot{C}Cl_2$	MNP	43
5	$CH_2=CHCCl_2F$	$\dot{C}Cl_3$	55—60	$CCl_3CH_2\dot{C}HCCl_2F$	MNB	$CCl_3CH_2CHCl\dot{C}ClF$	MNP	42
6	$CH_2=CHCHCl_2$	$\dot{C}Cl_3$	55—60	Unidentified	MNP	$CCl_3CH_2CHCl\dot{C}HCl$	MNP	42
7	$ClCH_2CHClCCl_3$	$P\dot{h}$	25	$ClCH_2C\dot{C}lCCl_3$		$ClCH_2CCl_2\dot{C}Cl_2$		14

are sufficiently stable for their study by EPR in the liquid phase at the usual temperatures [38-40]. The large selection of spin-trapping agents available makes the method virtually universal for the detection of a wide variety of radicals. The method is experimentally simple. It has been shown [14,41,42] that various radicals formed in the reaction system can be identified by employing the selectivity of the spin-trapping agents [34,43]. Thus in a series of reactions (Table 2, Nos. 3–6) rearranged radicals of the type $R\dot{C}Cl_2$, $R\dot{C}ClF$, and $R\dot{C}HCl$ were identified in experiments carried out in the presence of methylnitrosopropane $(CH_3)_3CNO$(MNP) as the spin-trapping agent. Non-rearranged radicals of the type $R\dot{C}HR$ could be identified by carrying out the same reactions in the presence of another spin-trapping agent, namely 2-methyl-2-nitrosobutan-3-one $CH_3COC(CH_3)_2NO$ (MNB); Table 2 shows that other applications of the selectivity of spin-trapping agents have also been made.

Particularly important results have been obtained by employing the EPR method in the study of the detailed mechanism of the rearrangement of $XCCl_2\dot{C}H_2$ radicals with 1,2-migration of chlorine. Hoag and Heiba [44] suggested (without carrying out their own experiments on this subject) that the rearrangement proceeds via an elimination–addition mechanism. Significant evidence in support of an intramolecular mechanism of this rearrangement has been adduced in a number of papers and reviews [4,5,13]; it can now be assumed that this has been rigorously demonstrated by EPR. [14,41] It has been shown in a number of instances [14] that the EPR spectra of the spin adducts of the radicals $RCCl_2\dot{C}Cl^1Cl^2$ with $(CH_3)_3CNO$ and other trapping agents contain signals which show that the Cl^1 and Cl^2 atoms are equivalent in relation to the p_z orbital, when their environments in the nitroxy-radical are the same, but are non-equivalent when the environments are not the same. This observation has been used in the study of the rearrangements of radicals (IX) to (X) and of (XI) to (XII):

$$\underset{\text{(IX)}}{CCl_3\dot{C}HCl} \rightarrow \underset{\text{(X)}}{\dot{C}Cl_2CCl_2H} \quad \underset{\text{(XI)}}{CCl_3\dot{C}ClCH_2Cl} \rightarrow \underset{\text{(XII)}}{\dot{C}Cl_2CCl_2CH_2Cl} \ .$$

Radicals (IX) and (XI) were generated by the abstraction of hydrogen from CCl_3CH_2Cl or $CCl_3CHClCH_2Cl$ by phenyl radicals (Table 2, Nos. 2 and 7). The radicals C_6H_5 were obtained by the method of Razuaev et al. [45] The parameters of the EPR spectra of the spin-adducts of these radicals with MNP are presented in Table 3. In both cases the EPR spectra consist of a superposition of signals due to the spin-adducts of both non-rearranged and rearranged radicals with $(CH_3)_3CNO$. It was found that the β-chlorine atoms in the spin-adducts of the rearranged radicals are non-equivalent with respect to the $2p_z$ orbital of the nitrogen atom; this establishes unambiguously that the migrating chlorine atom in the radical is located in the plane of the $2p_z$ orbital of the carbon atoms to which the chlorine migrates and hence the intramolecular nature of the rearrangement is demonstrated [14,41].

Table 3. Parameters of the EPR spectra [14] of the nitroxy-radicals $RN(\dot{O})C(CH_3)_3$.

Non-rearranged radical	a_N, G	a_{Cl}, G	Rearranged radical	a_N, G	a_{Cl}, G
$CCl_3\dot{C}HCl$	17.9	4.8	$\dot{C}Cl^1Cl^2CCl_2H$	12.7	Cl^1 4,5; Cl^2 1,0
$CCl_3\dot{C}ClCH_2Cl$	12.1	4.0	$\dot{C}Cl^1Cl^2CCl_2CH_2Cl$	12.2	Cl^1 4,0; Cl^2 1,0

2. The 1,2-Migration of Bromine

The rearrangement of radicals with 1,2-migration of bromine was described for the first time by Skell et al. [46] in 1961 in relation to the photochemical chlorination of t-butyl bromide and isopropyl bromide by t-butyl hypochlorite with formation of 1-bromo-2-chloro-methylpropane and 1-bromo-2-chloropropane respectively. Rearrangements of this type have been investigated vigorously in recent years in the photochemical halogenation of bromohydrocarbons [20,44,46-52]. The primary radical rearranges to a tertiary radical with a higher yield than in the rearrangement to a secondary radical, which is consistent with the general behaviour [4]. Thus the rearrangement in the photochemical chlorination of t-butyl bromide, resulting in 1-bromo-2-chloro-2-methylpropane, proceeds with a nearly quantitative yield [46], while the rearrangement of isopropyl bromide under the same conditions gives rise to 1-bromo-2-chloropropane with a yield which is only 15% of theoretical [46]. It is noteworthy that in the series of examples investigated a formally unusual rearrangement of more stable radicals to less stable radicals takes place, which undoubtedly reflects the characteristics of the mechanism of this rearrangement. For example, the photochemical bromination of labelled butyl bromide,

$$CH_3CH_2CH_2CH_2^{82}Br \xrightarrow{Br^\cdot} CH_3CH_2CH^{82}BrCH_2Br \ ,$$

results in the conversion of a secondary radical into a primary radical [48].

There are no reliably established examples of rearrangements with migration of bromine to a more remote radical centre [53]. It has been suggested [31] that the

formation of $[(CH_3)_2CBrCH_2CBr_2]_2SO_2$ in the reaction of bis(tribromomethyl)sulphone with isobutene includes a stage where the radicals rearrange with 1,5-migration of bromine:

$$CBr_3SO_2CBr_2CH_2\dot{C}(CH_3)_2 \rightarrow \dot{C}Br_2SO_2CBr_2CH_2CBr(CH_3)_2 \ .$$

The mechanism of the rearrangement of radicals with 1,2-migration of bromine. The problem of the mechanism of the rearrangement of radicals with 1,2-migration of bromine proved to be closely related to the problem of the anchimeric cooperation in the elimination of the β-carbon atom in bromoalkanes and the formation of a bromine bridge in the radical. In this case the rearrangement involves the mechanism

$$R_2CBr-CHR'_2 \xrightarrow[-HX]{+X^\cdot} R_2C(\overset{\cdot}{Br})-CR'_2 \xrightarrow{+X^\cdot} R_2CX-CR'_2Br \ .$$
X = Cl, or Br

The anchimeric cooperation in the abstraction of a β-hydrogen atom and the formation of a bridged radical is also indicated by data published in a number of reports [46, 48,50,54,55].

The high selectivity of the radical hydrogenation of bromohydrocarbons with formation of vicinal dihalogeno-derivatives, noted by many workers [46-52], confirms the bridged structure of bromoalkyl radicals. However, in another series of studies data have been adduced in support of an elimination–addition mechanism for reactions of this kind [40,56,57]. It has also been stated [48] that there are no data whereby one could distinguish the situation where the intermediate bromoalkyl radicals are static symmetrical bridged structures from one where there is an equilibrium conversion of a pair of asymmetric intermediate bridged species ($\tau_{1/2} \simeq 10^{-11}$ s).

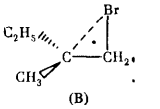
Data have also been presented in support of the intermediate formation of the classical radicals $\dot{C}-C-Br$ [44,52] (see also Cristol et al.[58]). It is noteworthy that none of the above series of studies can explain without contradictions all the observed facts in terms of a single reaction mechanism [47,58].

The attempts to obtain the EPR spectra of β-bromoalkyl radicals in the liquid phase were unsuccessful even at $-120°C$ owing to the instability of these radicals [59]. The reaction of HBr with *cis*- and *trans*-but-2-ene as well as certain other unsaturated compounds has been investigated [60] by EPR at 70 K; the authors have attributed the observed spectra to the radical-adducts of bromine and but-2-ene. These spectra are compatible with the idea that bridged radicals of the type

$$CH_3CH(\overset{\cdot}{Br})-CHCH_3$$

are formed. However, the possibility of another assignment of the spectral signals and of a different interpretation of the results of Abel and Peitte [60] has been pointed out [61].

Chemical data, in particular the results of the study of the stereochemistry of the photochemical halogenation of bromoalkanes, support the bridged structure of the β-bromoalkyl radicals. Thus the liquid-phase photobromination of the optically active 1-bromo-2-methylbutane with bromine [62] yielded 1,2-dibromo-2-methylbutane with a high optical purity. The rearrangement in the photochlorination of (+)(2*S*)-bromobutane by t-butyl hypochlorite leads to the formation of optically active 1-bromo-2-chlorobutane [48]. Analogous results were obtained in a study [63] where the authors were able to trap an asymmetric intermediate radical (B) in the form of a product $C_2H_5CD.(CH_3)CH_2Br$ of the addition of deuterium (from DBr) to the bridged radical with retention of the initial configuration to an extent greater than 96%:[63]


(B)

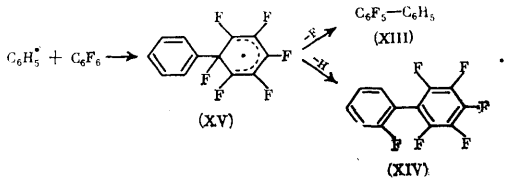
These facts cannot be accounted for either by an elimination-addition mechanism or by the hypothesis of the classical structure of β-bromoalkyl radicals, since in these cases racemic compounds should have been obtained [48,64,65]. From a study of the tritium isotope effect in the reaction

$$R\dot{C}HCH_2Br + TBr \rightarrow RCHTCH_2Br + \dot{B}r \ , \qquad (3)$$

it was concluded [66] that the presence of Br in the β-position relative to the radical centre lowers the energy of the bromoalkyl radical, possibly by the formation of a radical analogue of the cyclic bromonium ion.

3. The Migration of Fluorine

Very little is known about the possibility of the rearrangement of radicals with migration of fluorine. It has been shown [67,68] that the interaction of phenyl radicals, generated by the decomposition of nitrobenzene, with perfluorobenzene in the gas phase at 600°C leads to a mixture of products, the principal of which are pentafluorobiphenyl(XIII) and hexafluorobiphenyl (XIV):

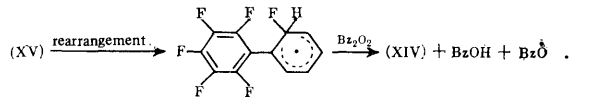


Compound (XIII) is formed via the usual aromatic substitution mechanism involving the addition of a phenyl radical to perfluorobenzene with formation of the radical-adduct (XV) containing the cyclohexadienyl group, this being followed by the elimination of fluorine. The formation of compound (XIV) has been explained [67,68] by the intramolecular substitution of hydrogen in the benzene ring by fluorine. Thus in this instance an unusual rearrangement of radical (XV) takes place with migration of fluorine to the neighbouring aromatic ring and not to the radical centre. The homolytic abstraction of fluorine from radical (XV) in this process is unusual. In the liquid phase hexafluorobiphenyl is not formed in the reaction of perfluorobenzene with benzoyl peroxide.

The reaction of hexafluorobenzene with phenyl radicals generated from other sources (phenylazotriphenylmethane [69], benzoyl peroxide [69,70]) has been investigated [69,70] at much lower temperatures. A detailed study has been made of the decomposition of benzoyl peroxide in hexafluorobenzene at 78.2°C [the kinetics of the decomposition process, the influence of the addition of benzoic or *p*-fluorobenzoic acid and the ratio of the yields of (XIII) and (XIV)]. This study established that the elimination of

fluorine from the σ-complex (XV) takes place in the reaction with an arenecarboxylic acid with formation of compound (XIII), HF, and ArCOO. This reaction of carboxylic acids is of independent interest.

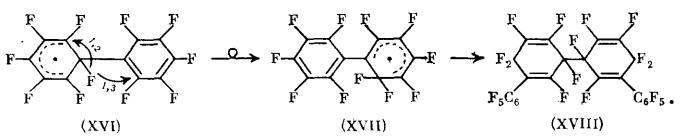
A study[70] of the kinetics of the decomposition of Bz_2O_2 in hexafluorobenzene showed that, together with the dissociation of the O–O bond (a first-order reaction), sensitised decomposition of the peroxide takes place (a reaction order of 1.5). The formation of the rearranged product (XIV) and benzoic acid is coupled with the last reaction:



It has been stated[70] that the high-boiling fraction apparently contains isomeric dodecafluorotetrahydroquaterphenyls. Thus a deeper understanding of the individual stages of this interesting process has been achieved. The mechanism of the stage involving a rearrangement with migration of fluorine to the neighbouring ring is at present least clear.

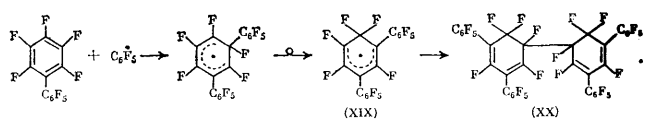
The interaction of hexafluorobenzene with nitromethane at 550°C gives a low yield of hexafluorotoluene $C_6F_5CH_2F$; this process also involves a rearrangement stage[71]. It is of interest to note that at 150°C hexafluorobenzene interacts with acetyl peroxide without a rearrangement; the main reaction products are 4,4′-dimethylperfluoro-1,1′,4,4′-tetrahydrobiphenyl and its isomers[72].

Interesting results were obtained in a study of the reaction of perfluorobenzene with perfluorobenzoyl peroxide[73] (in sealed tubes at 200°C). The pure substance (XVIII) was isolated from the mixture of products on repeated recrystallisation; according to ^1H and ^{19}F NMR, the substance is 3,3′-bis(pentafluorophenyl)perfluoro-1,1′,4,4′-tetrahydro-1,1′-biphenyl. The authors suggest that the radical-adduct (XVI), formed as a result of the addition of the pentafluorophenyl radical to perfluorobenzene, rearranges to the perfluorophenylcyclohexadienyl radical (XVII), whose dimerisation leads to compound (XVIII):



The authors[73] state that this example does not permit a choice between 1,2- and 1,3-migration of fluorine in the radical-adduct (XVI), since the rearranged radical-adduct (XVII) is formed in both cases.

The study of the reaction of pentafluorobenzoyl peroxide with decafluorobiphenyl[74] and with octafluorotoluene[75] suggested the migration of fluorine to a neighbouring carbon atom. For decafluorobiphenyl, the reaction involves the mechanism[74]



Perfluoro-3,3′,5,5′-tetraphenyl-1,1′,2,2′-tetrahydro-1,1′-biphenyl (XX), which is formed by the recombination of radicals (XIX), was isolated from the mixture of isomers.

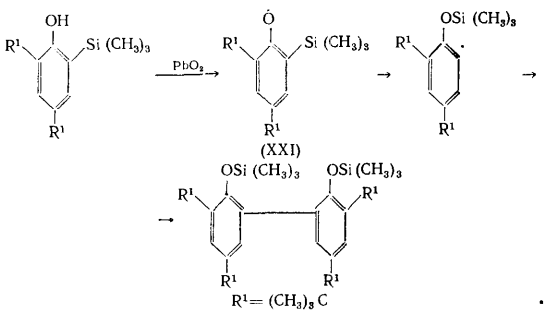
III. REARRANGEMENTS OF RADICALS WITH MIGRATION OF ORGANOELEMENTAL GROUPS

One of the new fields of study involving the rearrangement of radicals comprises the detection and investigation of rearrangements where the migrating group incorporates a heteroatom, which participates in the formation of a transition state via free *d* orbitals or π-bonds. Instances of the migration of the R_3Si, R_3Ge, RC(O)O, RCO, and RS groups are examined below.

1. The Migration of Silicon-, Germanium-, and Tin-Containing Groups

An interesting series of studies have been devoted to the investigation of the radical 1,3-migration of the R_3Si group from carbon to oxygen. This rearrangement was apparently first discovered in the thermolysis of 2,4,6-bis(trimethylsilyl)phenol,[76,77] but a detailed and systematic investigation of this type of migration of the trialkylsilyl group was undertaken by Razuvaev and coworkers[78–83], who demonstrated, in particular, the radical mechanism of this process.

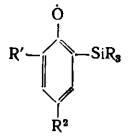
The oxidation of 4,6-di-(t-butyl)-2-trimethylsilylphenol by PbO_2 or $K_3Fe(CN)_6$ in a neutral solvent in the absence of oxygen leads to the formation of the relatively stable phenoxy-radical (XXI), whose rearrangement and subsequent recombination give a quantitative yield of the corresponding dimers[78,79]:



The formation of the phenoxy-radical was observed by EPR (1 : 2 : 1 triplet spectrum due to splitting by the *meta*-protons of the aromatic ring). It was shown that the R_3Si group migrates exclusively from the *ortho*-position[80] regardless of the number and positions of other such groups in the ring.

There is no rearrangement (1,5-, from C to O) in 2,6-di-t-butyl-4-trimethylsilylphenol. On the other hand, the degree of rearrangement involving the migration of the R_3Si group from the *ortho*-position depends significantly on the nature of the substituents in the *para*-position[81]. The yields of the rearranged dimers of 2,6-bis(trimethylsilyl)-4-R-phenols are presented in Table 4. The absence of a rearrangement for R = CH_3 (Table 4) is attributed to the lower stability of the corresponding rearranged phenoxy-radical[81]. When the capacities of the $(C_6H_5)_3Si$ and $(CH_3)_3Si$ groups for migration were compared, an unusual dependence of the rate on the nature of the substituent R′ in the phenoxy-radical (XXII) was

noted[82].



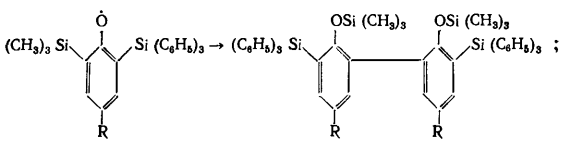
(XXII)
$R^2 = (CH_3)_3C$

Thus, when $R' = CH_3$, the trimethylsilyl group (where $R = CH_3$) migrates to the oxygen atom and the triphenylsilyl group ($R = C_6H_5$) does not migrate; for $R' = Br$, the opposite behaviour is observed.

Table 4. The 1,3-migration of the $(CH_3)_3Si$ group in 4-R-2,6-$[(CH_3)_3Si]_2C_6H_2\dot{O}$.

R	CH_3	$CH(CH_3)_2$	$C(CH_3)_3$	$Si(CH_3)_3$
Yield of rearranged dimer, %	0	77	95	81

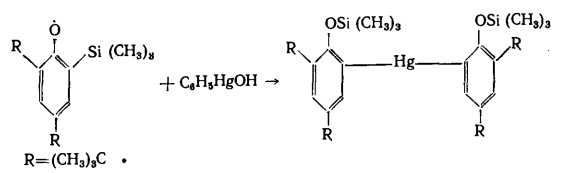
A phenoxy-radical in which there is a possibility of a competitive migration of these groups has also been investigated:



(XXIII)
$R = (CH_3)_3C$.

The dimer (XXIII) is the only reaction product, i.e. under these conditions only the $(CH_3)_3Si$ group migrates.

Only silylphenoxy-radicals capable of rearrangement yield mercurated derivatives on interaction with C_6H_5HgOH:[83]



$R = (CH_3)_3C$.

Less sterically hindered phenols react without rearrangement.

The radical mechanism of the migration of organosilicon radicals and the significant role of bulky *ortho*-substituents, ensuring the stability of the phenoxy-radical, was undoubtedly demonstrated in this series of studies; an intramolecular process mechanism appears to be extremely probable. On the other hand, the nature of the transition state and the special role of the silicon atom are still obscure, in view of the fact that the carbon analogues of silicon-containing phenoxy-radicals do not rearrange under these conditions with migration of $C(CH_3)_3$ groups[81].

The study of the decomposition of silicon-containing peracid esters made it possible to observe, together with other processes, the 1,4-migration of the trimethylsilyl group from carbon to oxygen[84]:

$$(CH_3)_3SiCH_2CH(CH_3)C(O)OOC(CH_3)_3 \xrightarrow[CCl_4]{120-130^\circ} \rightarrow (CH_3)_3SiCH_2CH(CH_3)COO\cdot \xrightarrow{\text{rearrangement}} \cdot CH_2CH(CH_3)COOSi(CH_3)_3 \rightarrow \rightarrow CH_2{=}C(CH_3)COOSi(CH_3)_3 .$$

An analogous rearrangement was noted also for organogermanium compounds[85]:

$$(C_2H_5)_3GeCH_2CH_2C(O)OOC(CH_3)_3 \xrightarrow[CCl_4]{100-105^\circ} \rightarrow (C_2H_5)_3GeCH_2CH_2COO\cdot \xrightarrow{\text{rearrangement}} \cdot CH_2CH_2COOGe(C_2H_5)_3 \rightarrow \rightarrow CH_2{=}CHCOOGe(C_2H_5)_3 .$$

The acrylate formed as a result of the rearrangement has been obtained in a yield of ~10%.

Such parallelism in the ability of organosilicon and organogermanium radicals to migrate has been discovered also in the rearrangement of *N,O*-bisorganosilyl(germyl)-hydroxylamines with 1,2-migration from oxygen to nitrogen[86]. When $RSi(CH_3)_2NHOSi(CH_3)_2R$ [$R = CH_3$, C_2H_5, $C(CH_3)_3$, or C_6H_5] was irradiated in the presence of t-butyl peroxide, only the signal due to the nitroxy-radical (XXV) (triplet with $a_N = 6.5$ G) was observed:

$$\underset{\text{(XXIV)}}{RSi(CH_3)_2\dot{N}OSi(CH_3)_2R} \rightarrow \underset{\text{(XXV)}}{[RSi(CH_3)_2]_2N\dot{O}} . \quad (4)$$

The signal of the non-rearranged radical (XXIV) could not be detected even at −80°C. For the analogous germyl radical $[RGe(CH_3)_2]_2N\dot{O}$, the EPR signal consisted of a triplet with $a_N = 8.8$ G.

The migration of the $(CH_3)_3Si$ and $(CH_3)_3SiSi(CH_3)_2$ groups from silicon to the sulphur atom in the thiyl radicals (XXVI) and (XXVII) proceeds under mild conditions in the presence of radical initiators[87]:

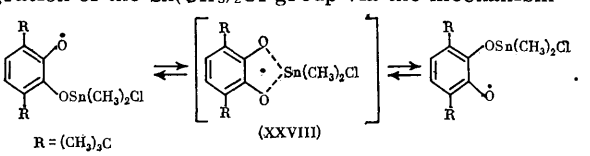
$$[(CH_3)_3Si]_2Si(CH_3)SH \xrightarrow{Bz_2O_2} \underset{\text{(XXVI)}}{[(CH_3)_3Si]_2Si(CH_3)\dot{S}} \rightarrow$$

$$\rightarrow (CH_3)_3Si\dot{S}i(CH_3)SSi(CH_3)_3 \rightarrow (CH_3)_3SiSiH(CH_3)SSi(CH_3)_3 . \quad (5)$$

$$\underset{\text{(XXVII)}}{(CH_3)_3SiSi(CH_3)_2Si(CH_3)_2\dot{S}} \rightarrow \dot{S}i(CH_3)_2SSi(CH_3)_2Si(CH_3)_3 . \quad (6)$$

Both reactions are inhibited by hydroquinone. It has been suggested that the transfer of the radicals $(CH_3)_3Si\dot{S}i(CH_3)_2$ proceeds via a three-membered transition state.

In stable phenoxy-radicals there is reversible 1,4-migration of the $Sn(CH_3)_2Cl$ group via the mechanism[88]



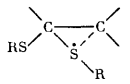
$R = (CH_3)_3C$ (XXVIII)

The rearrangement was inferred from the EPR spectra.

2. The Migration of Oxygen- and Sulphur-Containing Groups

When the behaviour of O- and S-containing radicals is compared in rearrangements, one often has to emphasise differences rather than similarities in the capacity of O- and S-containing groups for migration in the radical. The

differences are apparently due to the ability of the sulphur atom to interact with the neighbouring carbon atom carrying the unpaired electron (possibly with participation of the *d* orbitals of sulphur). Hence arose the hypothesis of the three-membered transition state (XXIX) in the 1,2-migration of the RS group:



(XXIX)

1,2-Migration is in fact characteristic of radicals containing two geminal alkylthio- or arylthio-groups in the β-positions relative to the radical centre.

On the other hand, a rearrangement of radicals with migration of alkoxy- or aryloxy-groups has not been described. The 1,2-migration of the acyloxy-group has been most thoroughly investigated for oxygen-containing radicals; it is suggested that the rearrangement proceeds via a five-membered transition state with unpairing of the electrons in the π-bond of the C=O group.

On the other hand, the preferential migration to the vicinal carbon atom is a common characteristic of these rearrangements.

(a) Migration of Oxygen-Containing Groups

Migration of the acyloxy-group. The Unusual behaviour of the acyloxy-group in the radical rearrangement consists in the fact that the oxygen atom of the carbonyl group can participate in the formation of an intermediate transition state.

The rearrangement of radicals with 1,2-transfer of the AcO group was first demonstrated in 1967 for the addition of radical species to α,α-dimethylallyl acetate[89,90]:

$$(CH_3)_2C(OAc)CH{=}CH_2 + \dot{R} \rightarrow \underset{(XXX)}{} \rightarrow (CH_3)_2C(OAc)\dot{C}HCH_2R \begin{cases} \rightarrow (CH_3)_2C(OAc)CH_2CH_2R \\ \rightarrow (CH_3)_2\dot{C}CH(OAc)CH_2R \xrightarrow{RH} \underset{(XXXI)}{(CH_3)_2CHCH(OAc)CH_2R} \end{cases} \quad (7)$$

The degree of rearrangement then depends significantly on the nature of the addend RH and the structure of the non-rearranged radical. A rearrangement involving migration to a more remote radical centre does not occur, nor does it take place when one of the methyl groups has been replaced by hydrogen. If a malonate ester [R = $CH(CO_2.C_2H_5)_2$] is used as an addend, then the yield of the rearranged acetate (XXXI) is 95%, while with R = $CH(CN).CO_2C_2H_5$ it is only 25–30%, which the authors attribute to the different efficiencies of these compounds as hydrogen donors. For the relatively ineffective cyclohexane (R = C_6H_{11}), it was possible to detect the acetate (XXXI) (yield 4%) even when one of the CH_3 groups in the initial acetate (XXX) has been replaced by hydrogen[90].

It is of interest to note that the analogous reaction with the thioloacetate $(CH_3)_2C(SAc)CH = CH_2$ takes place without a rearrangement even for cyclohexane[90].

The migration of the acetoxy-group was observed by studying the radical decarbonylation of 3-acetoxy-3-methylbutanal in the presence of benzoyl peroxide[91]:

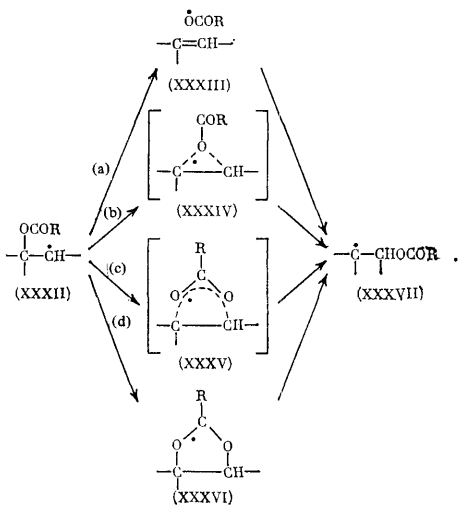
$$(CH_3)_2C(OAc)\dot{C}H_2 \rightarrow (CH_3)_2\dot{C}CH_2OAc \quad .$$

Further studies of rearrangements of this type were devoted mainly to the investigation of the mechanism of the migration of the AcO group[92,93]. In principle, several mechanisms can be put forward for the 1,2-transfer of the acyloxy-group[92].

One of these (*a*) involves elimination-addition and two others (*b* and *c*), involve the transfer of the AcO group via a three-membered (XXXIV) or five-membered (XXXV) unstable transition state; the last mechanism (*d*) involves 1,2-transfer with formation of the 1,3-dioxolanyl radical (XXXVI) as an intermediate.

The elimination–addition mechanism has been rejected[94] because it had been established previously[95] that the free acetoxy-radical ȮC(O)R rapidly decomposes to CO_2 and $\dot{C}H_3$ even in the presence of effective radical trapping agents. In addition it has been shown[91] that a decrease of the concentration of the initial aldehyde (in the decarbonylation reaction) promotes a relative increase in the yield of the rearranged product, which is also inconsistent with an elimination–addition mechanism.

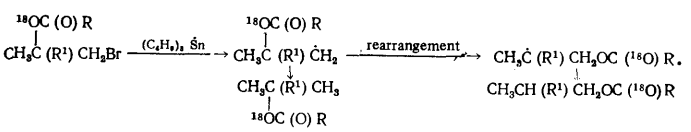
The spectrum of the dioxolanyl radical (XXXVI), known to have been obtained (Scheme 8) was detected by EPR;[92] it did not contain signals which could be attributed to the rearranged radical (XXXVII).



(8)

On the other hand, by studying the abstraction of hydrogen by OH radicals from $(CH_3)_3COAc$, Beckwith and Tivdal[96] obtained a set of signals characterising the radicals $\dot{C}H_2C(CH_3)_2OAc$ and $(CH_3)_2\dot{C}CH_2OAc$, but did not observe any signs of the formation of the cyclic radical (XXXVI).

The choice between pathways *b* and *c* was made in favour of *c* in the study of radicals labelled with ^{18}O. It was shown[92] that the rearrangement involves the inversion of the label in the molecule of the labelled specimen:



An analogous result was obtained with a specimen labelled at the oxygen atom of the carbonyl group. Naturally, in the three-membered transition state (XXXIV) (Scheme 8) there should be no inversion.

The only example of the 1,3-migration of the acetoxy-group has been found[97] in the oxidation of γ-acetoxy-carboxylic acid (XXXVII):

$$\begin{array}{l} \mathrm{AcOCRR^1CH_2CHR^2COOH} \xrightarrow[60^\circ]{S_2O_8^{2-}} \\ \quad (\mathrm{XXXVIII}) \\ \rightarrow \mathrm{AcOCRR^1CH_2\dot{C}HR^2} \left\{ \begin{array}{l} \longrightarrow \mathrm{AcOCRR^1CH_2CH_2R^2} \\ \longrightarrow \mathrm{\dot{C}RR^1CH_2CHR^2OAc} \rightarrow \mathrm{CHRR^1CH_2CHR^2OAc} \end{array} \right. \\ \quad (\mathrm{XL}) \qquad\qquad\qquad\quad (\mathrm{XLI}) \qquad\quad (\mathrm{XXXIX}) \end{array} \quad (9)$$

The yield of the isomerised ester (XXXIX) ranges from 3 to 10%, depending on the nature of the substituent: 3% for $R = R^1 = H$, $R^2 = CH_3$; 6% for $R = R^2 = H$, $R^1 = CH_3$; 10% for $R = R^1 = CH_3$, $R^2 = H$; i.e. the greater the difference between the stabilities of the initial radical (XL) and the rearranged radical (XLI), the greater the degree of rearrangement.

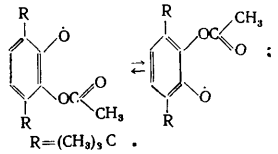
The migration of the acyl group. In the decomposition of the peracid ester (XLII) [Scheme (10)] both the non-rearranged ketone (XLIII) and the ketone (XLIV), corresponding to the radical (XLV) formed as a result of the 1,2-migration of the acyl group[98] in the radical (XLVI), were identified among the reaction products:

$$\begin{array}{l} \mathrm{CH_3C(O)CR^1R^2CH_2C(O)OOC(CH_3)_3} \xrightarrow{130^\circ} \\ \quad (\mathrm{XLII}) \\ \rightarrow \mathrm{CH_3C(O)CR^1R^2\dot{C}H_2} \left\{ \begin{array}{l} \longrightarrow \mathrm{CH_3C(O)CR^1R^2CH_3} \\ \qquad (\mathrm{XLIII}) \\ \longrightarrow \mathrm{\dot{C}R^1R^2CH_2C(O)CH_3} \xrightarrow{DH} \mathrm{CHR^1R^2CH_2C(O)CH_3} \end{array} \right. \\ \quad (\mathrm{XLVI}) \qquad\qquad\qquad\quad (\mathrm{XLV}) \qquad\quad (\mathrm{XLIV}) \end{array} \quad (10)$$

For $R^1 = R^2 = H$, there is no rearrangement; for $R^1 = R^2 = CH_3$, the ratio of the yields (XLIV)/(XLIII) is approximately unity; for $R^1 = CH_3$ and $R^2 = C_6H_5$, the ratio (XLIV)/(XLIII) $\simeq$ 1.3. In the generation of the radicals (XLVI) in the $CH_3C(O)C(CH_3)_2CH_2X + R_3SnH + R^1\dot{O}$ system this ratio is 0.4 for X = Br and $R = C_6H_5$, 0.15 for X = Cl and $R = C_6H_5$, and 0.18 for X = Cl and $R = C_4H_9$ respectively.

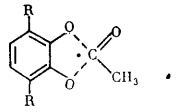
The most probable mechanism of the rearrangement involves the formation of the unstable cyclopropoxy-radical in the transition state. However, it has been suggested[99] that the isomerisation can proceed, at least partially, via an elimination–addition mechanism. In the case of the radical $CH_3C(O)CH_2\dot{C}H_2$ the authors were able to detect the formation of $CH_3\dot{C}O$ and ethylene. The radical $CH_3\dot{C}O$ reacted with cyanopyridine to give a substitution product. The radicals (XLVI, $R^1 = H$, $R^2 = CH_3$) and (XLV, $R^1 = H$, $R^2 = CH_3$) were also detected as substitution products. Thus the occurrence of the reaction via two mechanisms simultaneously can be postulated.

For stable radicals, the reversible 1,4-migration of the acetyl group was observed by EPR:[100]



$R = (CH_3)_3C$.

It was suggested[100] that the migration proceeds via the cyclic transition state



(b) Migration of Sulphur-Containing Groups

The rearrangement of radicals with 1,2-migration of the thiyl group was discovered for the first time in 1963 in relation to the isomerisation of acetone diphenyl mercaptole under the influence of t-butyl peroxide[101]:

$$\begin{array}{l} \mathrm{CH_3C(SC_6H_5)_2CH_3} \xrightarrow[140^\circ]{(CH_3)_3C\dot{O}} \mathrm{CH_3C(SC_6H_5)_2\dot{C}H_2} \longrightarrow \left[\begin{array}{c} \mathrm{CH_3C(SC_6H_5)CH_2} \\ \mathrm{SC_6H_5} \end{array} \right] \longrightarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (\mathrm{ILVII}) \\ \longrightarrow \mathrm{CH_3\dot{C}(SC_6H_5)CH_2SC_6H_5} \xrightarrow{H^\bullet} \mathrm{CH_3CH(SC_6H_5)CH_2SC_6H_5} \end{array} \quad (11)$$

A radical chain mechanism of the process was demonstrated and evidence was adduced in support of an intramolecular mechanism of the transfer of the RS radical[101]. On heating in the absence of an initiator, acetone mercaptoles do not isomerise. It has been suggested[4] that the migration of the RS group proceeds via a cyclic three-membered transition state (XLVII) as a result of the ability of sulphur to delocalise the unpaired electron at the neighbouring carbon atom.

Soon examples of the thermal isomerisation of mercaptoles in the absence of radical initiators were described[102,103]. Thus, on heating without the peroxide, acetophenone diphenyl mercaptole gives rise to 1,2-diphenylthioethylbenzene (~10%), but the main products are α-phenylthiostyrene and diphenyl disulphide:

$$\mathrm{C_6H_5C(SC_6H_5)_2CH_3} \xrightarrow{135^\circ} \mathrm{C_6H_5C(SC_6H_5)=CH_2} + \mathrm{C_6H_5CH(SC_6H_5)CH_2SC_6H_5} + (\mathrm{C_6H_5S})_2 .$$

A similar behaviour was observed also for pinacolone diphenyl mercaptole; the formation of appreciable amounts of an unsaturated compound, diphenyl disulphide, and traces of thiophenol justified the hypothesis[103] that thermal rearrangements proceed via an elimination–addition mechanism. Depending on the reaction conditions and the structure of the initial mercaptoles, both mechanisms can apparently operate. The pathway leading to the initiation of thermal rearrangement and the problem of the possible chain transfer by the extremely stable benzyl radicals $C_6H_5\dot{C}(SC_6H_5)CH_2SC_6H_5$, formed as a result of the rearrangement, remains obscure.

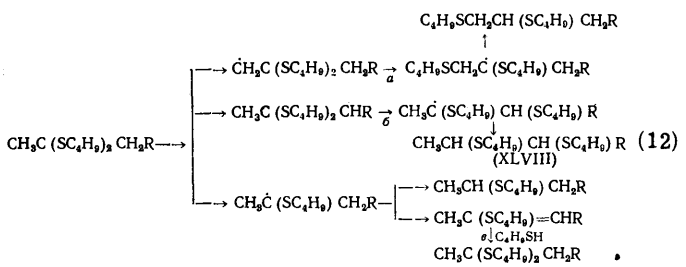
The use of the EPR method with spin trapping agents in the study of the rearrangement of mercaptoles capable of thermal isomerisation (in the absence of an initiator) confirmed the radical nature of the process and led to the determination of the nature of the initiating radicals[104]. Together with signals due to the known radicals, the spectrum obtained on irradiation of acetophenone diphenyl mercaptole in the presence of 2-methyl-2-nitrosopropane (as the spin trapping agent), showed the presence of a triplet (a = 25.7 G), which was assigned to the spin-adduct of the oxy-radical $C_6H_5C(\dot{O})(SC_6H_5)CH_3$, formed as a result of the oxidation of the $C_6H_5\dot{C}(SC_6H_5)CH_3$ radicals formed initially in the thermolysis. The oxy-radicals abstract hydrogen from the methyl group of the mercaptole regenerating the initial radical $C_6H_5C(SC_6H_5)_2\dot{C}H_2$. It has been shown[102] that acetophenone diphenyl mercaptole is capable

of initiating the rearrangement of acetone diphenyl mercaptole in the absence of a peroxide. Presumably the rearrangement is in this case initiated by the oxy-radicals formed in the thermolysis of the acetophenone mercaptole.

The mechanism of the 1,2-migration of thiyl radicals as well as the influence of various factors on the course of the rearrangement of mercaptoles became the subject of further discussion and investigations carried out in recent years in relation to the mercaptoles of higher symmetrical and asymmetric ketones[105,106], cyclic ketones[107], and ketones containing functional groups[108]. In a few studies it has been suggested[94,109] that the radical migration of the RS groups takes place in all cases via an elimination–addition mechanism. The authors based their conclusion on the absence of a rearrangement, which they demonstrated in the reaction of α,α-dimethylallyl phenyl sulphide with free radicals, where the intermediate radical fragments with elimination of the RS group:

$$(CH_3)_2C(SC_6H_5)-CH=CH_2 + R^{\cdot} \rightarrow (CH_3)_2\dot{C}CHCH_2R(SC_6H_5) \rightarrow (CH_3)_2C=CHCH_2R.$$

However, subsequent studies showed that such analogy between monosulphides and *gem*-bis-sulphides is insufficiently well-founded. The intramolecular mechanism of the 1,2-migration of the thiyl group was clearly demonstrated in a study of the isomerisation of the dibutyl mercaptole of acetoacetic ester (R = $CO_2C_2H_5$) in the presence of t-butyl peroxide [Scheme (12)], where the authors obtained for the first time a complete material balance and were able to trace the fate of all the radicals formed[108]:



(12)

Here there is a possibility of two competitive pathways involving the migration of RS groups (*a* and *b*); it was shown that the migration proceeds preferentially to the carbon of the methyl group (*a*). Presumably this pathway in the transition of the RS group is related to the more favourable conditions for the formation of a transition state of type (XLVII) with participation of the terminal CH_2 group. Special experiments have shown that the addition of butanethiol to ethyl 3-butylthiocrotonate [Scheme (12), pathway *c*] results in a low yield of only the initial ketone mercaptal and not the rearranged product (XLVIII). Thus, by virtue of the mode of addition, the elimination–addition mechanism cannot account for the formation of the products of the rearrangement in this instance.

Acetone mercaptoles isomerise also on irradiation with ultraviolet light[110]. When the reaction was carried out at different temperatures (70° and 140°C), it was found that an increase of temperature leads to a sharp increase of the yield of the rearrangement product (almost by a factor of 20 for acetone diphenyl mercaptole). Instead of the expected formation of $CH_3CH(SC_4H_9)CH_2SC_6H_5$ (via an elimination–addition mechanism), in the isomerisation of $CH_3C(SC_6H_5)_2CH_3$ in the presence of 20 mole% $CH_3C(SC_4H_9) = CH_2$ the process was found to be inhibited and the unsaturated sulphide was fully consumed in side reactions. The study of the rearrangement of mixed ketone mercaptoles (acetone butyl phenyl and butyl *p*-tolyl mercaptole) initiated by t-butyl peroxide showed[111] that, together with symmetrisation, there is a rearrangement of both symmetrical and mixed mercaptoles; in the latter case the rearrangement proceeds mainly as a result of the migration of the arylthio-group.

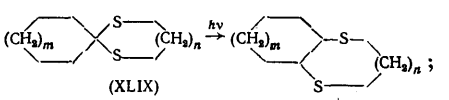
In the isomerisation of 2-butanone and 2-hexanone dibutyl mercaptoles under the influence of t-butyl peroxide at 140°C the butylthio-group migrates in two directions—to the neighbouring methyl and methylene carbon atoms[105]. In both examples [Scheme (12), R = CH_3 or C_3H_7] the 1,2-bis-sulphides $C_4H_9SCH_2CH(SC_4H_9)CH_2R$ are formed preferentially, i.e. the migration proceeds to a large extent towards the carbon of the methyl group.

The study of the isomerisation of butanone diphenyl mercaptole by EPR in the presence of 2-methyl-2-nitrosopropane as the spin trapping agent made it possible to detect the spin-adducts of the initial radical $CH_3C(SC_6H_5)_2.\dot{C}HCH_3$ and the rearranged radical $CH_3\dot{C}(SC_6H_5)CHCH_3$.[112]
SC_6H_5

It is noteworthy that the migration of the RS group to a radical centre more remote than a neighbouring centre has not so far been observed.

For the mercaptoles of cyclic ketones, the yield of the rearrangement products is influenced significantly by the ring size[107]. Thus the yield of 1,2-bis(butylthio)cycloalkane is twice as high for a six-membered ring as for a five-membered ring. This rearrangement proceeds solely on heating with t-butyl peroxide. On the other hand, thermolysis yields mainly 1-butylthiocyclohex-1-ene and butanethiol. The absence of rearrangement products on thermolysis and ultraviolet irradiation shows that the reverse addition of butanethiol to the unsaturated compound does not occur under the given conditions, which rules out an elimination–addition mechanism.

The study of the photochemical isomerisation of cyclic ketone mercaptoles (XLIX, *a* = *d*) showed that the possibility of isomerisation depends significantly on the ring size[113]:



(a) $m = 1$, $n = 0$; (b) $m = n = 0$, (c) $m = n = 1$, (d) $m = 0$, $n = 1$. (13)

In the reaction involving ethylene mercaptoles (XLIX, *a* and *b*) the main process is the splitting off of ethylene sulphide with formation of cyclic thiones. The propylene mercaptoles (XLIX, *c* and *d*) undergo a kind of isomerisation under these conditions with transfer of one of the geminal sulphur atoms to a neighbouring carbon atom [Scheme (13)]. It has been suggested that the reaction proceeds in this case via an elimination–addition mechanism. However, the usual intermolecular transfer is naturally ruled out.

The study of the rearrangement of radicals has come to be a permanent and very important topic in the modern chemistry of free radicals. The possibility of rearrangements must be reckoned with in studies on new reactions and also in industrial radical processes such as chlorination, oxidation, reduction, polymerisation, telomerisation, and many other processes.

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NMR Study of Equilibrium Intermolecular Exchange Processes Involving Univalent Organometallic Groups of the Type R_nM, Containing an Atom of a Heavy Non-transition Metal from Periods V and VI

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The results of NMR studies of intermolecular exchange reactions accompanied by the rupture of a metal - carbon or metal - heteroatom bond for the case where the role of the metal is played by a univalent organometallic group containing a heavy non-transition metal as central atom have been systematised. The bibliography contains 146 references.

CONTENTS

I.	Introduction	840
II.	Intermolecular exchange of the metal - metal type taking place with the rupture of metal - carbon bonds (C,C-exchange of organometallic groups)	841
III.	Intermolecular exchange of organometallic groups, taking place with metal - heteroatom bond rupture	844
IV.	C,E-exchange of organometallic groups	848
V.	Exchange between organometallic groups and a proton, taking place with the rupture of a cationic particle - heteroatom bond (E,E-exchange within the framework of exchange of the metal - proton type)	849

I. INTRODUCTION

Exchange reactions of type (1) represent one of the most widely encountered types of chemical transformation, characteristic of inorganic, organic, and organometallic compounds:

$$AX + BY \rightleftarrows BX + AY \ . \qquad (1)$$

In the field of organic compounds, the exchange reactions include replacement at a carbon atom, and hydrogen exchange[1-5]. In the field of inorganic compounds, exchange reactions include ligand exchange at a metal or non-metal atom, where the ligands may be anions or neutral molecules[3]. A specific feature of exchange reactions in inorganic compounds is that, since many metal compounds are insoluble in aprotic organic solvents, ligand exchange is studied in an aqueous medium, and the materials studied have been mainly complex compounds[6-9]. Finally, for organometallic compounds of non-transition and transition metals, exchange reactions (1) involve chiefly intermolecular transfer of the organometallic groups from one ligand to another with the rupture of metal–carbon or metal–heteroatom σ- or (π-) bonds.

The present review deals chiefly with exchange reactions of the type:

$$R_nMX + R_nM^*Y \rightleftarrows R_nM^*X + R_nMY \ , \qquad (2)$$

where R_nM and R_n^*M are univalent organometallic groups.

The choice of this process is determined by the following considerations. Exchange reactions of type (2) in organometallic derivatives of EH-acids (where the anionic residue E contains as connecting atom the elements C, N, O, S, etc.) formally resemble hydrogen exchange in the EH-acids themselves:

$$HX + H^*Y \rightleftarrows H^*X + HY \ . \qquad (3)$$

In both cases there is intermolecular exchange of species of cationic type. The specific feature of this exchange is that both R_nM and H are able to act as unshared electron pair acceptors, exhibiting a greater or lesser coordinating power, depending on the nature of the partner. The lability of M–X bonds usually decreases with decrease in their polarity. It is therefore appropriate to determine the specific features of the migrating power of organometallic groups compared with the hydrogen atom with the minimum difference in the polarity of the corresponding bonds. This condition is satisfied to the greatest extent by the heavy non-transition metals of periods V and VI. Unlike the metals of periods II–IV, the heavy non-transition metals form bonds of low polarity, and the electronegativity differences between them and the hydrogen atom are appreciably smaller than those between the hydrogen atom and the metals of the higher periods.

In this connection, the present review deals with the intermolecular exchange of univalent particles of cationic type, containing heavy non-transition metals of periods V and VI.

In the analysis of reactions of type (2) it is possible to concentrate attention on the dynamics of either the anionic or the cationic groups. In the first case, the exchange reactions (2) and (3) can be divided into three types[10]:

metal–metal (M–M*) exchange;
metal–proton (M–H) exchange;
proton–proton (H–H*) exchange.

In the second case, reactions (2) can be classified as follows:

exchange of the carbon–carbon type (C,C-exchange of organometallic groups);
heteroatom–heteroatom exchange (N,N-, O,O-, S,S-, etc. exchange);
carbon–heteroatom exchange (C,N-, C,O-, C,S-, etc. exchange).

The chief method of studying exchange processes in many cases is by NMR[11-15], which makes it possible to obtain the quantitative characteristics of exchange reactions and to analyse the mechanism by which they take place. The "popularity" of NMR is related to the fact that exchange reactions of the type being considered often take place at rates commensurate with the time scale of this method. Even in those cases where the rate of exchange is low on the NMR time scale, the method makes it possible to determine the composition of the reaction mixture without resorting to preparative isolation of the components.

In recent years, NMR has been widely used to study the migrating power of organometallic groups in exchange reactions of type (2), and in particular to study exchange in which $R_nM = R_n^*M$. In this case the NMR method makes it possible to study exchange reactions both for non-degenerate exchange ($X \neq Y$) and for degenerate exchange ($X = Y$). In the case of non-degenerate exchange (2), evidence of the process may be provided by the changes in the shielding of the groups R of R_nM, which should in principle be different. In the study of degenerate exchange, the shielding of the groups of the group R will not change in the course of the exchange. If however the metal contains isotopes having half-integral spin, and the substituent contains indicator atoms or groups of atoms, it is possible to reach conclusions regarding the characteristic features of the exchange (2) from the presence or absence of spin–spin coupling between them and the nucleus of the metal atom.

Most discussion in the literature has dealt with the spin–spin coupling of the nuclei of the metal with a proton in the fragment M–E–C–H (where E = O, S, N) in organometallic derivatives in which the M–E bond is the most labile part of this fragment. However, although the existence of spin–spin coupling in this fragment makes it possible to conclude that intermolecular exchange is slow (on the NMR time scale), the absence of this type of interaction in the NMR spectrum (without special search for it under conditions of slow exchange) is not a strict indication of a fast reaction.

II. INTERMOLECULAR EXCHANGE OF THE METAL–METAL TYPE TAKING PLACE WITH THE RUPTURE OF METAL–CARBON BONDS (C,C-EXCHANGE OF ORGANOMETALLIC GROUPS)

Intermolecular exchange processes accompanied by the rupture of an R_nM-C bond and the formation of a new bond of this type have been most widely studied for M = Cd[16–25] and Tl[26–31] and to a lesser extent for M = Hg[32–35]. For other metals, only fragmentary data are available.

1. Exchange in Derivatives of Metals of Group IIb

In a series of organic compounds of the group IIb metals, the exchange reactions being considered can be represented in general form as follows:

$$RM_1{-}R' + RM_2{-}R'' \rightleftarrows RM_1{-}R'' + RM_2{-}R' \quad . \qquad (4)$$

Degenerate intermolecular exchange ($M_1 \neq M_2$, $R' = R''$), accompanied by the rupture of M–C bonds, has been most widely studied for the methyl derivatives of cadmium (reaction (4), $M_1 = M_2 = Cd$ and $R = R' = R'' = CH_3$)[18,19,21,24,36–39]. It has been shown that under certain conditions (medium, temperature, concentration) the exchange reaction (4) in $(CH_3)_2Cd$ takes place at rates comparable with the NMR time scale, that this reaction shows second-order kinetics (in ether), and that its activation energy is 15.6–17.0 kcal mole^{-1} (in toluene) or 5.6–7.0 kcal mole^{-1} (in THF, triethylamine, ether). The reaction rate increases considerably when basic compounds are added to solutions of $(CH_3)_2Cd$ in inert media.

A study of the ^1H NMR spectra of diethyl- and di-isobutylcadmium in toluene and pyridine[14] revealed $^{111/113}Cd$ satellites, which became slightly broader with increase in temperature, again possibly indicating that the exchange reaction (4) takes place in these compounds.

In contrast to the case of the dialkyl compounds of cadmium, the ^1H NMR spectrum of $(H_2C{=}CH)_2Cd$, because of rapid exchange, does not show $^{111/113}Cd{-}C{-}^1H$ spin–spin coupling in ether and hydrocarbon media[32]. At the same time, $^{111/113}Cd{-}C{-}^{19}F$ satellites are observed for solutions of $(CF_3)_2Cd$ in THF, indicating fairly slow exchange (4) in this compound[23].

In contrast to the cadmium compounds, the complete organometallic mercury compounds R_2Hg and $RHgR'$ show $^{199}Hg{-}C{-}^1H$ (R = CH_3, C_2H_5, $C_6H_5CH_2$, $H_2C{=}CH$, etc.)[40–44], $^{199}Hg{-}^{13}C$,[45–47] and $^{199}Hg{-}C{-}^{19}F$ (R = CF_3, C_2F_5, $F_2C{=}CF$, etc.)[48–51] spin–spin coupling over a wide range of conditions. This feature is evidently related to the high stability of the Hg–C bonds with respect to exchange in these compounds.

The Hg–C bond is activated by including, in symmetrical organo-mercury compounds, multiple bonds in the β-position relative to the Hg–C bond[52]. A ^1H NMR study of $(C_5H_5)_2Hg$ at room temperature and lower temperatures in weakly solvating solvents revealed rapid intermolecular exchange of C_5H_5Hg groups from one C_5H_5 group to another[35]. The rate of the process increases sharply with increase in temperature and (or) increase in the solvating power of the solvent:

$$C_6H_6 < R_2O < C_5H_5N < DMF < DMSO \ .$$

The earliest studies of non-degenerate exchange reactions in organic derivatives of group IIb metals by NMR were carried out by Allred and McCoy[16,17] for various mixtures of the type (4) (M_1 = Cd, M_2 = Zn or Hg, R = R′ = R″ = CH_3). These and subsequent studies[18,20,22,24,25] revealed the main characteristics of these non-degenerate C,C-exchanges of organometallic groups. It was suggested[16,17] that the averaging of the shielding of the methyl groups, observed in mixtures of dimethylcadmium and dimethylzinc, is due to the rapid exchange of CH_3M groups from one methyl group to another. The order of this reaction in all solvents except ethyl ether is 1.7 ± 0.3, and its rate is independent of the dielectric constant of the solvent, but depends on its donor power. This indicated that ionisation is not the rate-determining stage of the exchange reaction (4). When one of the components of the system is dimethylmercury, the exchange is slow on the NMR time scale[17,18].

Thus in alkyl derivatives of the group IIb metals, the reactivity of the M–C bonds in intermolecular exchange increases in the order: Hg–C ≪ Cd–C < Zn–C.

Another illustration supporting this conclusion is provided by data for $R_2'M + R_2''M$ mixtures (M = Cd and Hg). Thus a ^{113}Cd NMR study of an equimolar $(CH_3)_2Cd + (CH_3CH_2)_2Cd$ mixture showed[25] that the spectrum contains three $^{113}Cd\{^1H\}$ signals with intensity ratio 1 : 2 : 1; the central signal corresponds to the mixed derivative $CH_3CdC_2H_5$. This indicates that the rupture of the Cd–C bond is slow on the NMR time scale.

The NMR data for $R_2'Hg + R_2''Hg$ mixtures (R′ = $C_6H_5CH_2$, R″ = CH_3 or C_6H_5; R′ = CH_3, R″ = C_6H_5 or CF_3, etc.) indicate that the exchange leading to the formation of the compounds R′HgR″ can take place only when the corresponding mixtures are heated for a long time at a high temperature[43].

The dependence of the reactivity of the Cd–C bond in non-degenerate exchange (4) on the nature of R has been studied[20]. Thus for M_1 = Cd, M_2 = Zn, and R = R′ = R″ = $CH_2{=}CH$, the $M{-}CH{=}CH_2$ σ-bond is more labile than the $M{-}CH_3$ bond. A similar conclusion follows from the study of this reaction for $M_1 = M_2$ = Cd and R = R′ = CH_3;

$R'' = CH_2{=}CH$; or $R = R' = H_2C{=}CH$; $R'' = CH_3$.

2. Exchange in Derivatives of Group III Metals

Exchange reactions in organic derivatives of group III metals can be represented in general form as follows

$$R_2M{-}R + R_2M^*{-}R^* \rightleftarrows R_2M{-}R^* + R_2M^*{-}R \quad . \qquad (5)$$

Degenerate exchange in compounds of this type has been studied in most detail for trimethylthallium [26,27]. At low temperatures the ^1H NMR spectra of solutions of $(CH_3)_3Tl$ in CH_2Cl_2 or $C_6D_5CD_3$ show two signals of equal intensity, due to the splitting of the methyl protons on the thallium isotopes. With increase in temperature these signals become broader and merge, indicating that Tl–C bond rupture is fairly frequent on the time scale of the method. The reaction is of approximately second order, and its activation energy is 6 ± 1 kcal mole^{-1} in CH_2Cl_2 and 6.3 ± 0.5 kcal mole^{-1} in $C_6D_5CD_3$. When $C_6D_5CD_3$ is replaced by the solvating solvents $(CH_3)_2O$ and $(CH_3)_3N$, the rate of exchange decreases slightly [27]. It is suggested [27] that the mechanism of this intermolecular exchange involves the formation of a dimeric transition state.

Reaction (5) was also studied by ^1H NMR for $(C_2H_5)_3Tl$ and $(C_6H_5)_3Tl$. [26,27] For $(C_6H_5)_3Tl$, the following order of decrease in the exchange rate with increase in the solvating power of the medium was established:

$$CH_2Cl_2 > C_6D_6,\ (CH_3)_2O > (CH_3)_3N \quad .$$

Non-degenerate C,C-exchange involving groups containing indium or thallium has been comparatively little studied. Thus the formation of compounds of the type R_2TlR' and $RTlR'_2$ in R_3Tl and R'_3Tl mixtures has been detected by ^1H NMR for $R = CH_3$ and $R' = C_2H_5$. At room temperature, the exchange is rapid on the NMR time scale, whereas at low temperatures in CH_2Cl_2 the individual spectra of all possible compounds are observed [26]. NMR data have also been obtained for the exchange of groups in the system $(CH_3)_3Tl + (CH_3)_2Tl(HC{=}CH_2) + CH_3Tl(HC{=}CH_2)_2$. [27] The study of the last process established that the exchange of vinyl groups is more rapid than that of methyl groups.

NMR data [54–61] make it possible to reach conclusions regarding the limits of stability of Tl–C bonds in exchange reactions. Thus the ^1H NMR spectra of R_2TlX, where X represents electronegative substituents, at room temperature in different media show $^{203/205}Tl{-}C{-}^1H$, $^{203/205}Tl{-}C{-}C^1H$, and $^{203/205}Tl{-}^{13}C$ splitting, indicating that the Tl–C bond is stable under these conditions. This was confirmed [28] by a study of $(CH_3)_2TlX + (C_2H_5)TlX$ mixtures, which showed that the system does not contain mixed derivatives $(CH_3)(C_2H_5)TlX$.

Exchange with rupture of Tl–C bonds is not observed in various compounds of the type $(CH_3)_2Tl{-}R$, where $R = C{\equiv}CC_6H_5$ or C_5H_5. [30,31] There are few data on exchange reactions in derivatives of other group III metals. The intermolecular exchange (5) for $M_1 = In$ and $M_2 = Ga$ ($R = R' = R'' = CH_3$) is rapid on the NMR time scale even at $-65°$ in toluene [62]. A study of exchange in a $(CH_3)_3In + (CH_3)_6Al_2$ mixture in toluene [62] showed that the rate of this process depends on the reagent ratio but is independent of the concentration. This indicates that the reaction is not bimolecular, and that the exchange is preceded by the conversion of the $(CH_3)_6Al$ dimers into monomers, which limits the overall process.

3. Exchange in Mixtures of Derivatives of the Metals of Groups II and III

C,C-exchange of organometallic groups in mixtures of the alkyl derivatives of metals of groups IIb and III by NMR was first studied by McCoy and Allred [17]. In mixtures of $(CH_3)_2Cd$ and $(CH_3)_3Al$ in benzene at room temperature, methyl groups are exchanged (reaction (6), $M_1 = Cd$, $M_2 = Al$, $R = R' = R'' = CH_3$):

$$RM_1{-}R' + R_2M_2{-}R'' \rightleftarrows RM_1{-}R'' + RM_2{-}R' \quad . \qquad (6)$$

Important kinetic and thermodynamic data were obtained [20,24] for the case where $R = R' = R'' = CH_3$, $M_1 = Cd$, and $M_2 = In$ or Ga. In most cases the reaction is bimolecular, and $(CH_3)_2Cd$ exchanges with $(CH_3)_3In$ more slowly than with $(CH_3)_3Ga$. For $R = R' = R'' = CH_3$ and $M_1 = Cd$, $M_2 = Ga$ or $M_1 = Zn$, $M_2 = In$, [24] the rate of exchange decreases with increase in the coordinating power of the solvent.

4. Exchange in Derivatives of Group IVb Metals

M–C bonds, where M = Sn and Pb, are much more stable than the bonds formed by these metals with heteroatoms. Intermolecular C,C-exchange of organometallic groups in a series of organotin and organolead compounds has been detected by NMR only under catalytic conditions [63].

Under ordinary conditions, the NMR spectra of organotin and organolead compounds show $^*M{-}C{-}^1H$ ($^*M = {}^{119}Sn$ [64–67] and ^{207}Pb, [68,69]) $^*M{-}^{13}C$ (^{119}Sn, [70–72] ^{207}Pb [70,73,74]), $^*M{-}C{-}^{19}F$ (^{119}Sn, [65] ^{207}Pb [75]), etc. spin–spin coupling, indicating that the M–C bonds are stable on the NMR time scale.

One example of exchange accompanied by the rupture of an Sn–C bond is known, however: broadening of the signals of the $^{117/119}Sn$ satellites is observed [76] when $(CH_3)_3SnC{\equiv}CCF_3$ is dissolved in hexamethylphosphortriamide.

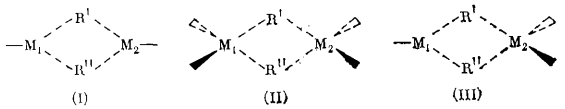
5. Mechanism of Intermolecular C,C-Exchange

The available data on exchange reactions accompanied by the rupture of metal–carbon bonds and subsequent intermolecular C,C-exchange of organometallic groups from one group to another can be summarised briefly as follows (Table 1).

1. All C,C-exchange reactions studied are bimolecular for derivatives of metals in groups IIb and III and for mixtures of group IIb and III derivatives [15,16,18,20,22,25,33]. The only exception is exchange in the $(CH_3)_3In + (CH_3)_6Al_2$ system, in which one of the reagents is a dimer [62].

2. C,C-exchange takes place in derivatives of metals of groups IIb (Cd) and III (In, Tl) and is practically unknown for metals of group IVb (Sn, Pb). For isostructural compounds in non-solvating solvents, the reaction rate is greatest for group III derivatives and lowest for derivatives of group IIb metals, and is intermediate in mixtures of compounds of metals of groups IIb and III. [20]

3. The rate of C,C-exchange is increased by solvating solvents of basic character in the case of group IIb metals (Cd) and decreased for group III metals (In, Tl) or mixtures containing a group III metal [18,21,24,20,27].



(I) (II) (III)

4. For organometallic derivatives of metals of groups IIb and III with identical groups but different metals, the rate of C,C-exchange decreases on going from compounds of metals of period V (Cd or In) to compounds of metals of period VI (Hg or Tl) [17,18,24,27,20]. For derivatives with identical metals but different groups, the rate of C,C-exchange increases on going to groups with more nucleophilic carbon atoms [27,22].

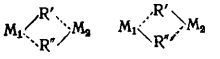
Table 1. Data on the intermolecular C,C-exchange of organometallic groups in a series of methyl derivatives of non-transition metals of periods V and VI: $(CH_3)_{n-1}M_1^*CH_3 + (CH_3)_{m-1}M_2CH_3 \rightleftharpoons (CH_3)_{n-1}M_1CH_3 + (CH_3)_{m-1}M_2^*CH_3$.

M_1	M_2	n	m	Solvent	E_a, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$S^{\neq}$, e.u.	Refs.
Cd	Cd	2	2	—	15.7	—	−9.8	21
Cd	Cd	2	2	THF	6.8	—	−28.3	21
Cd	Cd	2	2	$(C_2H_5)_3N$	6.9	—	—	24
Cd	Cd	2	2	$(C_2H_5)_2O$	5.6	—	−38	24
Cd	Zn	2	2	cyclo-$C_6H_{11}CH_3$	17.0	16.4	−3	20
Cd	Ga	2	3	cyclo-C_6H_{10}	6.7	8.1	−17	20
Cd	Ga	2	3	CH_2Cl_2	7.3	6.7	−19	20
Cd	Ga	2	3	toluene	7.0	6.4	−23	20
Cd	In	2	3	CH_2Cl_2	8.4	7.8	−14	20
Zn	In	2	3	CH_2Cl_2	5	—	—	24
Zn	In	2	3	$(C_2H_5)_2O$	9.1	8.5	−14	24
Zn	In	2	3	$(C_2H_5)_3$	16.3	15.7	+2	24
In	Ga	3	3		5	—	—	62
Tl	Tl	3	3	CH_2Cl_2	6	—	—	27
Tl	Tl	3	3	toluene-α-d_3	6.3	—	—	27

The basic hypothesis regarding the mechanism of intermolecular C,C-exchange in the reactions being considered usually assumes that the transition state has a four-unit structure [17,18,20,22,24,27,35].

Evidence in support of this suggestion is provided by the bimolecular character of all reactions for which the concentration dependence has been studied, and also by the negative entropy of activation of most exchange reactions (Table 1) [20,24].

The ease of formation of a cyclic transition state with delocalised bonds should be influenced significantly by the coordinating power of the metal atom and in particular by its ability to form cyclic associates. This is due to the fact that the organic groups R′ and R″ and the non-transition metals M_1 and M_2, following Henold and coworkers [20], can be regarded as Lewis bases and acids. On the other hand, a cyclic transition state is a structure intermediate between real or hypothetical cyclic associates:



Exchange between them must involve the overcoming of an energy barrier, the height of which determines the ease of formation of a cyclic transition state with delocalised bonds. For hydrogen-bonded associates, increase in the energy of the hydrogen bonds is accompanied by a decrease in the height of the barrier, and the state of the system approaches a state with delocalised bonds [77,78]. An analogous phenomenon should be observed for organometallic associates with increase in the intensity of coordination interactions. Thus the stable dimer of trimethylaluminium corresponds structurally to a cyclic transition state with delocalised bonds for exchange between two trimethylaluminium molecules [79].

It may therefore be expected that the ease of formation of the transition states (I)–(III) and the rate of exchange reactions will increase with increase in the coordinating power of the metal atom and the donor power of the groups R, including the case where associates are not formed in the solution of the compound R_mM. [17,80] Thus for example the order of change in the rate of exchange:

$$Zn + Cd > Cd + Cd \gg Zn + Hg,\ Cd + Hg,\ Hg + Hg;$$
$$In + Zn > In + Cd;$$
$$Ga + In > Tl + Tl$$

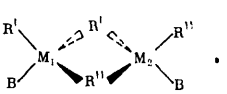
in methyl derivatives $(CH_3)_mM$ (m = 2 or 3) corresponds to the decrease in the acidity of the non-transition metals in isostructural compounds with increase in the period number [81,82] and also to the decrease in the ability of the structure to change from the normal configuration to that realised in the transition state [83]. The increase in the rate of exchange on going from methyl to vinyl compounds (M = Cd [22] or Tl [27]) is due to the greater ease of formation of transition states in the case of vinyl compounds due to the participation of the π-electrons of the vinyl group.

The available data on the influence of the medium on the rate of exchange reactions can also be explained if account is taken of the fact that in solvating media the compounds R_2M (M = Cd, Hg) and R_3M (M = In, Tl) are in the solvated state. The fundamental differences found in the analysis of C,C-exchange between compounds of the metals of groups IIb and III are evidently related to the following feature.

As a result of solvation (B is a unidentate solvent of basic character)

$$R_2M + 2B \rightleftarrows R_2M \cdot B + B \rightleftarrows R_2M \cdot 2B$$
$$R_3M + B \rightleftarrows R_3M \cdot B$$

derivatives of group IIb metals, which have two vacant orbitals, form solvates of two types, whereas compounds of group III metals with one vacant orbital form only one. The solvates $R_2M.2B$ and $R_2M.B$ with completely blocked vacant metal orbitals evidently cannot undergo exchange reactions because of the negligibly low acid strength of the metals†. At the same time the solvate $R_2M.B$ [84] may be more reactive than R_2M, since solvation leads to an increase in the basic strength of the group R, [85] and in addition the vacant metal orbital required for the formation of the transition state (IV) is preserved:



(IV)

Thus in solvating media the rate of exchange is limited by the formation of the transition state (IV) in the case of R_2M, and by the decomposition of the solvated species $R_3M.B$ in the case of R_3M. This last feature also applies to exchange in mixtures of derivatives of the metals of groups IIb and III, where the rate decreases in solvating solvents [24].

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† An example is provided by the complex $(CH_3)_2Cd.[(C_2H_5)_2NCH_2CH_2N(C_2H_5)_2]$, in which both vacant orbitals of cadmium are blocked, and which, because of its stability, can be isolated in the crystalline state [81]. These features explain why the ^1H NMR spectrum of a solution of $(CH_3)_2Cd$ in tetramethylethylenediamine clearly shows satellites due to $^{117/119}Cd$–C–H spin–spin coupling, indicating slow exchange of the methyl groups [37].

III. INTERMOLECULAR EXCHANGE OF ORGANOMETALLIC GROUPS TAKING PLACE WITH METAL–HETEROATOM BOND RUPTURE

1. N,N-Exchange of Organometallic Groups

For most metals except mercury [10,87,88] and tin [89-94], there are comparatively few published data on the NMR spectra of compounds containing the fragment $R_nM-N<$ which might give an indication of the range of lability of these bonds in exchange reactions of the type

$$R_nM—NR'R'' + R_nM^*—N^*R'R'' \rightleftarrows R_nM—N^*R'R'' + R_nM^*—NR'R'' \quad (7)$$

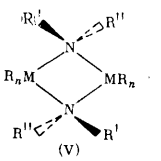
For mercury derivatives, there were until recently only fragmentary data on N,N-exchange of organomercury groups. Thus for $CH_3HgN(CF_3)_2$, $^{199}Hg-N-C-^{19}F$ spin–spin coupling was not detected, and this can be attributed to exchange of methylmercury groups between different $N(CF_3)_2$ groups [87].

Exchange reactions have been studied [10] in organomercury derivatives of substituted N-methylbenzenesulphonamides. In these compounds there is relatively rapid N,N-exchange of arylmercury groups (7) (R_nM = ArHg, $NR'R'' = N(CH_3)SO_2Ar'$). The reaction rate increases considerably with increase in the concentration of the organomercury derivative and decreases slightly when the solvent chloroform or chlorobenzene is replaced by the solvating pyridine.

Electron-accepting substituents in the arylmercury group increase the rate of the N,N-exchange of the arylmercury groups, and electron-donating substituents decrease it:

$$4\text{-}(CH_3)_2NC_6H_4 < 2,4,6\text{-}(CH_3)_3C_6H_2 < 4\text{-}CH_3OC_6H_4 < C_6H_5 < 4\text{-}ClC_6H_4 < 3,4,5\text{-}Cl_3C_6H_2.$$

These results indicate [10] that in sufficiently inert media, the mechanism of the N,N-exchange of arylmercury groups (7) is associative in character and is accompanied by the formation of a cyclic transition state (structure (V), R_nM = ArHg, $R' = CH_3$, $R'' = SO_2Ar'$).


(V)

In the ^1H NMR spectra of various compounds of the type $R_2TlN(CH_3)_2$, the $N(CH_3)_2$ group corresponds to a triplet signal, indicating splitting of the methyl protons not on one but simultaneously on two equivalent thallium nuclei [95,96]. This proves that this compound is dimeric in solution (structure (V), $R_nM = R_2Tl$, $R' = CH_3$) and that the Tl–N bonds are stable on the ^1H NMR time scale.

The N,N-exchange of organometallic groups has been studied to a slightly greater extent in organotin derivatives. A study of the ^1H NMR spectra of 20% solutions of organotin derivatives of diethylamine $R_3SnN(C_2H_5)_2$ in CCl_4 at room temperature revealed spin–spin coupling of the $^{117/119}Sn$ nuclei with the CH_2 protons in the diethylamino-group, indicating that the Sn–N bond has a fairly long lifetime [89,90]. It was later found, however, that the ^1H NMR spectrum of $(CH_3)_3SnN(CH_3)_2$, studied in the absence of solvent, does not show $^{117/119}Sn-N-C-^1H$ spin-spin coupling either at room temperature or at −50° [91] (or even at −68° [92]). The most acceptable explanation of these results is that there is rapid exchange of the organotin groups between the dimethylamino-groups (reaction (7), $R_nM = (CH_3)_3Sn$, $NR'R'' = N(CH_3)_2$). $^{117/119}Sn-N-C-^1H$ spin–spin coupling was subsequently observed [93] in the ^1H NMR spectra of 20% solutions of $R_3SnN(CH_3)_2$ in benzene.

The temperature dependence of the form of the signals due to $^{117/119}Sn-N-C-^1H$ coupling has been studied [92]. Comparison of the temperatures at which the signals of the tin satellites merge for different compounds revealed the influence of the nature of the organic group, attached to the tin atom, on the rate of exchange:

$$(C_4H_9)_3SnN(CH_3)_2 < (C_2H_5)_3SnN(CH_3)_2 < (CH_3)_3SnN(CH_3)_2 .$$

In the compounds $(CH_3)_3SnN(CH_2)_n$ with heterocyclic $N(CH_2)_n$ groups, $^{119}Sn-N-^{13}C$ spin–spin coupling was observed [94] only for $n = 5$ or 6, but not for $n = 2-4$, indicating that the Sn–N bonds have a comparatively short lifetime.

In a discussion of the mechanism of exchange accompanied by the rupture of Sn–N bonds [94], it was suggested that this exchange is a bimolecular process, involving the formation of intermediates of type (V) ($R_nM = R_3Sn$). Evidence in support of this is provided, for example, by the dimeric structure of the compound $(CH_3)_3SnN(CH_2)_2$ in solution [94].

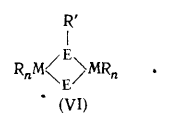
2. O,O-, S,S-, and O,S-Exchange of Organometallic Groups

Reactions of this type in the series of compounds being considered can be expressed as follows (E = O or S):

$$R_nM—ER' + R_nM^*—E^*R' \rightleftarrows R_nM—E^*R' + R_nM^*—ER' \quad (8)$$

They have been studied in most detail for organotin compounds [90,97-102] and less fully for derivatives of mercury [102-105], thallium [28,96,106-108], and lead [102,109,110].

Thus a study of solutions of the compounds C_6H_5HgOR' did not detect $^{199}Hg-O-C-^1H$ spin–spin coupling in any case [103], indicating that in CH_2Cl_2 at 33.5°, O,O-exchange of phenylmercury groups from one OR′ group to another is fairly rapid on the ^1H NMR time scale (reaction (8), $R_nM = C_6H_5Hg$, E = O). It was suggested that the reaction mechanism involves an associative scheme with the intermediate formation of dimers of type (VI), where E = O and $R_nM = C_6H_5Hg$.


(VI)

A ^1H NMR study of the phenylmercury derivative of toluene-ω-thiol [102] showed that the spectrum of solutions of this compound does not show $^{199}Hg-S-C-^1H$ spin–spin coupling at −40° (in chlorobenzene or pyridine) or even at −110° (in a $CH_2Cl_2 + CHCl_3$ mixture), indicating fairly rapid S,S-exchange of the phenylmercury groups (reaction (8), $R_nM = C_6H_5Hg$, $ER' = SCH_2C_6H_5$). Similar results were obtained in a study of the S,S-exchange of organomercury groups in mixtures of the compounds $t\text{-}C_4H_9HgSCH_3 + t\text{-}C_4H_9HgSCH(CH_3)C_6H_5$. [104] In this case the rate of the S,S-exchange of the organomercury groups in relatively inert media is so great that the rate of this bimolecular process can be decreased only at ~ −140°.

Data on the O,O- and S,S-exchange of organothallium groups R_2Tl have been published [28,96,106-108]. At room temperature the ^1H NMR spectra of many compounds of the type $(R_2TlX)_2$ (structure (VI), $R_nM = R_2Tl$), the signals due

to the spin–spin coupling of the protons of the R groups with ^{203}Tl and ^{205}Tl nuclei are broadened considerably and often are not resolved.

With decrease in the temperature of a solution of $[(CH_3)_2TlOC_2H_5]$ in $C_6D_5CD_3$,[108] the ^1H NMR spectrum shows broadening of the signals of the CH_3Tl groups. With further cooling of the solution below −10°, however, the signals of the methyl protons again become narrow and at −60° acquire the same form and width as at room temperature. A characteristic feature is that the $^{203/205}Tl-C-^1H$ spin–spin coupling constant is the same at +39° and at −60°. In the discussion of this phenomenon, the authors of Refs. 96 and 103 examined several possible associative exchange mechanisms, which reduce to the same form of exchange between the dimeric and monomeric state of the derivative being analysed.

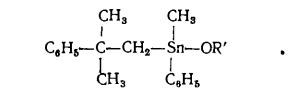
For the compounds R_3MER' (M = Pb, Sn; E = O, S) the exchange reactions with the rupture of M–O bonds have been least studied for the lead derivatives. Thus the ^1H NMR spectra of solutions of R_3PbOR' in CCl_4[109] do not show $^{207}Pb-O-C-^1H$ spin–spin coupling. Similar results were obtained in Ref. 110. Davies and Puddephat[109] suggested that this phenomenon is related to rapid exchange of organometallic groups from one OR′ group to another.

A study of the ^1H NMR spectra of organotin alkoxides of the type R_3SnOR' in CCl_4 at room temperature[90] did not detect $^{117/119}Sn-O-C-^1H$ spin–spin coupling. It was suggested that this result is due not to exchange but to the ionic character of the Sn–O bonds. Subsequent temperature studies of the ^1H NMR spectra of a number of organotin compounds containing an Sn–O bond[99–101] made it possible to observe this spin–spin coupling and hence to establish that the absence of $^{117/119}Sn$ satellites from the NMR spectra of R_3SnOR' derivatives in a number of cases is due not to the ionic character of the Sn–O bond but to the rapid exchange of the organotin groups from one oxygen atom to another (reaction (8), $R_nM = R_3Sn$, E = O). The rate of exchange increases in the order[99]:

$$CH_2C(CH_3)_3,\ CH(C_6H_5)_2,\ CH(CH_3)_2 < CH_2C_6H_5 < C_2H_5 < CH_3.$$

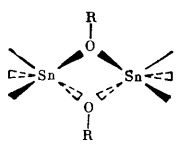
It was suggested that the exchange involves a bridged dimer (VI) ($R_nM = R_3Sn$, E = O).

The influence of a number of factors on the mechanism of exchange accompanied by the rupture of Sn–O bonds has been studied[100]. A study was made of the exchange reactions in compounds (VII); in solutions of these compounds in benzene, exchange of OR′ groups may be accompanied by inversion of the configuration of the tin atom[101].



R=CH₃, i-C₃H₇, t-C₄H₉, C₆H₅ (VII)

The rate of exchange of OR′ groups is not equal to the rate of inversion, that is not every exchange act is accompanied by inversion of the configuration of the metal atom. The nature of the group R′ has a greater influence on the rate of exchange than on the rate of inversion. A probable transition state for both processes may be the dimeric cyclic intermediate (VIII), the formation and decomposition of which take place with preservation of the configuration of the metal atom.

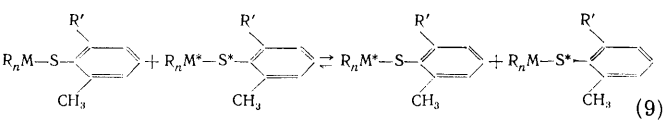


(VIII)

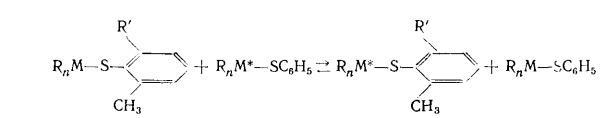
A study of the ^1H NMR spectra of the compound $(CH_3)_3SnSCH_3$ in chloroform[111] showed that the signals due to $^{117}Sn-S-C-^1H$ and $^{119}Sn-S-C-^1H$ spin–spin coupling are not resolved. Abel and Brady[112], in a study of this compound in a 30% solution in CCl_4, on the contrary, observed these signals separately; when even very small quantities of impurity (such as, for example, acids and thiols) are present in the solutions, however, the ^{117}Sn and ^{119}Sn satellites are not resolved; this is due to the catalysis of reaction (8) ($R_nM = (CH_3)_3Sn$, E = S, R′ = CH_3) by the impurities.

A number of subsequent papers give data on the values of $^3J(^{119}Sn-S-C-^1H)$[113] and $^2J(^{119}Sn-S-^{13}C)$[94] in R_3SnSR' compounds; the very fact that these data were obtained indicates that the Sn–N bonds in them have a fairly long lifetime. In particular, the study of the ^1H NMR spectra of the individual compounds $R_nMSCH_2C_6H_5$ or their mixtures in chlorobenzene and pyridine at different temperatures ($R_nM = (C_6H_5)_3Pb$ or $(C_6H_5)_3Sn$) did not detect any signs of exchange reactions of type (8).[102] Available data on the lability of the bonds M–O and M–S are too fragmentary to permit a comparison of the mobility of univalent organometallic groups with different metals for a fixed element E or to estimate the influence of the nature of the element E on the mobility of the organometallic groups of each type. A systematic examination of this problem was begun only recently[10,102,114–117].

Thus the dependence of the lability of the M–S bonds in thiophenol derivatives on the nature of the organometallic group has been studied[102,114,115] for the reactions



(9)



R′ = H or CH_3; $R_nM \neq R_nM^*R_nM$ and $R_nM^* = C_6H_5Hg$, $(C_6H_5)_3Pb$, $(C_6H_5)_3Sn$, $(C_6H_5)_2Sb$, $(C_6H_5)_4Sb$. (10)

The data[102,114,115] on the S,S-exchange of organometallic groups in these mixtures established the following regular features: a) the rate of the S,S-exchange increases when chlorobenzene is replaced by pyridine; b) the increase in the steric hindrance when a proton as R′ is replaced by a methyl group is accompanied by a decrease in the rate of exchange; c) the ability of organometallic groups to undergo intermolecular exchange in chlorobenzene increases in the order:

$$(C_6H_5)_3Sn < (C_6H_5)_2Sb \sim (C_6H_5)_3Pb < C_6H_5Hg < (C_6H_5)_4Sb\ .$$

These regular features are for the most part preserved[117] for O,O-exchange of organometallic groups in substituted phenols:

$$R_nM-OAr + R_nM^*-O^*Ar \rightleftarrows R_nM-O^*Ar + R_nM^*-OAr$$
$$R_nM \neq R_nM';\ R_nM \text{ and } R_nM^* = C_6H_5Hg,\ (C_6H_5)_3Pb,\ (C_6H_5)_3Sn,\ (C_2H_5)_3Sn\ . \quad (11)$$

As in the case of thiophenols, the C_6H_5Hg group has the highest mobility, and the $(C_6H_5)_3Sn$ group the lowest mobility in the exchange reaction (11). The rate of the process increases both with increase in the electron-acceptor

properties of the group Ar and when chloroform as solvent is replaced by pyridine. Steric hindrance, and also the presence, in the ortho-positions, of substances capable of intramolecular coordination interaction with the metal, on the other hand, decrease the rate of the O,O-exchange.

Data obtained by Kravtsov and coworkers [102] were interpreted on the basis of an associative exchange mechanism with the intermediate formation of cyclic four-unit transition states with delocalised bonds:



3. Exchange of Organometallic Groups Between Halogen Atoms

In the study of dynamic processes accompanied by the rupture of metal–halogen bonds, it is only in the case of Hal = F that it is possible to use NMR, which can be used successfully for derivatives of the type M–ER where E = O or S, and M–NR′R″, where E = N or P (analysis of the form of the signals corresponding to the spin–spin coupling *M–*E, *M–E–C–^{1}H, *M–E–^{13}C, *M–E–^{1}H, etc.). Thus in a study of the ^{1}H NMR of the compounds R_3SnF (R = CH_3, C_2H_5) in methanol solution [108], ^{1}H–C–Sn–^{19}F spin–spin coupling was not reported, although its value in $[C_6H_5CH(CH_3)_2CH]_3SnF$, measured later [119], was fairly high (~ 5 Hz). The absence of splitting can be attributed to F,F-exchange of organotin groups:

$$R_nM{-}X + R_nM^*{-}Y \rightleftarrows R_nM^*{-}X - R_nM{-}Y$$

$$R_nM = [C_6H_5CH(CH_3)_2CH_2]_3Sn,\ X = Y = F \quad , \qquad (12)$$

In this connection, in the study of halogen exchange in series of organometallic compounds, extensive use is made of the examination of the non-degenerate exchange of organometallic groups in mixtures of compounds with different halogen atoms (reaction (12), X ≠ Y = Hal, R_nM = RHg [42,43,120–122] or R_3Sn [123–128]). Another method makes it possible to study degenerate exchange in the case where the compound being studied contains a chiral (or prochiral) atom, inversion at which, detected by NMR, can in principle be related to reaction (12) (X = Y = Hal, R_nM = R_3Sn, etc. [125,129–134]).

In the ^{1}H NMR spectra of solutions of individual compounds of the type RHgI and RHgBr (R = CH_3,[42,43] $C_6H_5CH_2$,[43] $H_2C{=}CH$,[120] etc.), the satellites due to ^{199}Hg–C–^{1}H spin–spin coupling are either broadened or completely absent [42,43,120]. To explain this phenomenon it was first suggested [42,43,120] that in solutions of these compounds, fast exchange with rupture of C–Hg bonds takes place. Subsequent studies showed, however, that there is insufficient evidence for these suggestions. In particular, it has been found [53] that the C–Hg bond in alkyl derivatives of mercury is fairly stable and that exchange accompanied by its rupture cannot take place in fractions of a second.

The study of compounds RHgI [32,121,135] shows that the broadening in the NMR spectra of mercury satellites is due not to exchange but to relaxation effects‡. Thus in later studies [121,122] of exchange in organomercury layers, the results were interpreted in terms of halogen exchange.

Thus Hatton and coworkers [42], in a study of the ^{1}H NMR spectra of an equimolar mixture of methylmercury halides (X = Cl, Y = I) in pyridine at room temperature observed an averaged picture. Similar results were obtained in a study of the NMR spectra of ternary mixtures (RHgCl + RHgBr + RHgI; R = CH_3 or $C_6H_5CH_2$).[43] In mixtures of type (12) for R_nM = CH_3Hg, X = Cl or Br, and Y = I in DMF, exchange is rapid even at −71°.[122]

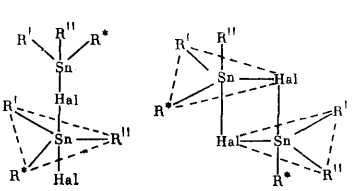
The reactivity of organotin compounds R_3SnX in halogen exchange reactions has been studied fairly frequently in recent years. In discussion relating to the interpretation of NMR data on halogen exchange in a series of organotin derivatives, many aspects of the problem became evident—the complexity of this reaction, and also a number of characteristic features of the compounds R_3SnX, which distinguish them from other derivatives R_nMX. Up to the present, however, there is still lack of agreement regarding the mechanism of this process.

A number of studies of the degenerate exchange of organotin groups between halogen atoms have been carried out for compounds of the type R′R″R*SnHal, in which the tin atom is chiral (R′ ≠ R″ ≠ R*) and the carbon group R* has a prochiral centre containing groups suitable for NMR study [$(CH_3)_2CH$, $C_6H_5(CH_3)_3CCH_2$, $C_6H_5CH_2$, $(CH_3)_2CHCH_2$, etc.] [129–131,192]. For these compounds in solution there is ready rapid inversion of the geometric configuration of the tin atom. There may be several reasons for this inversion: intermolecular exchange of organotin groups between halogen atoms is the most probable, but not the only explanation (reaction (12), R_nM = R′R″R*Sn, X = Y = Hal).

The conclusion that the observed phenomenon is of intermolecular origin is confirmed by the fact that in all cases, increase in concentration is accompanied by an increase in the rate of the process. The exchange involves the tin–halogen bond, since when the halogen atom in R′R″R*SnHal is replaced by a carbon group the dynamics are no longer recorded by NMR [130,131,137–139].

Direct proof has been obtained [131] for the relationship between the inversion of the tin atom and the exchange of the halogen atom in the compounds R′R″R*SnHal. The NMR study of the compounds (Hal = Cl and I, R* = C_6H_5·$(CH_3)_2CCH_2$, R′ = CH_3 and R″ = $C_6H_5CH_2$) showed that the rates of intermolecular exchange are exactly equal to the rates of inversion at the tin atom, and these two processes possibly take place by the same mechanism.

In a more detailed discussion of the associative mechanism of the exchange of halogens in the compound R′R″R*SnHal, accompanied by racemisation of the asymmetric tin atom, two versions were considered [131], with one or two bridging halogen atoms:



which agree with the bimolecular character of the process.

The non-degenerate exchange of anionic residues in the compounds R_3SnX (reaction (12), X ≠ Y, R_nM = R_3Sn) including the case where at least one of the substituents X or Y is a halogen atom, has been studied by NMR chiefly for systems with R = CH_3. [123–128,140] A NMR study of mixtures of these compounds (Y = Cl, Br, I) [123] showed that the rate of reaction (12) for the organotin halides

‡ The broadening of the mercury satellites in CH_3HgSCN has been shown [136] to be due to the presence of traces of CH_3HgI, used [42] to prepare methylmercury thiocyanate. The ^{1}H NMR spectrum of the compound CH_3HgSCN, obtained from methylmercury chloride, did not contain any sign of broadening of the mercury satellites [136].

changes in the order:

$$Cl + I < Br + I < Cl + Br \ .$$

Subsequently, several groups of workers made more detailed studies of the exchange reaction (12) in trimethyltin derivatives [124-126]. Thus Redl and Winokur [124], in a study of this reaction in cyclohexane (X = Cl, Y = I) found that with increase in temperature from 33° to 95°, the apparent rate constant of the reaction does not increase, but decreases§. Moreover, the order of the reaction with respect to each of the components is different, is not integral, and changes considerably with change in temperature. These results [124] indicate that in mixtures of organotin compounds, the kinetics of reaction (12) are complex. The authors cited believe that different types of associative equilibria, preceding the actual exchange, may be established in the solution:

$$2\,(CH_3)_3SnBr \overset{K}{\rightleftarrows} [(CH_3)_3SnBr]_2$$
$$(CH_3)_3Sn^*I + [(CH_3)_3SnBr]_2 \rightleftarrows (CH_3)_3Sn^*Br + (CH_3)_3SnBr + (CH_3)_3SnI \ . \quad (13)$$

The rate of exchange is given by the expression:

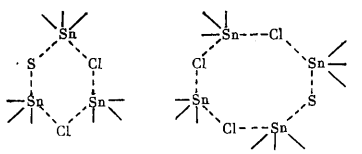
$$v = k_{app}[(CH_3)_3SnI]\,[(CH_3)_3SnBr]^2 = kK\,[(CH_3)_3SnI] \cdot [(CH_3)_3SnBr]^2 \quad (14)$$

Since the experimentally determined order of the reaction with respect to $(CH_3)_2SnBr$ is 2.6, it is possible that the exchange act is preceded by the formation of not only dimers but also associates with a larger number of units. Increase in temperature on the one hand should increase the rate of exchange by increasing k, but on the other hand will lead to a decrease in the concentration of associates (decrease in K in Eqn. [14]). If the absolute magnitude of the last effect is greater than that of the first, the overall rate of the reaction should decrease with increase in temperature.

Later, a ^1H NMR study for $R_nM = (CH_3)_3Sn$, X = Cl, and Y = I in toluene [125] showed that the overall order of reaction (12) at 27° is approximately three, again indicating a possible associative mechanism, although the rate of this reaction in the range from −70° to 30° does not decrease with increase in temperature, as shown in Ref. 124, but increases. At higher temperatures, however, the ^1H NMR spectrum did not show temperature reproducibility. The rate of exchange increases considerably on going from toluene to pyridine, whereas when Y = I is replaced by $Y = SC_6H_5$ or $C{\equiv}CC_6H_5$, the rate of exchange decreases. Reaction (12) was subsequently studied for the case where one of the anionic groups contains a sulphur atom ($Y = SCH_3$ [127] and SC_6H_5 [140,141]).

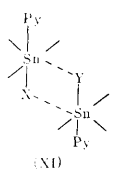
When X = Cl and $Y = SCH_3$, [127] the exchange reaction (12) in methylene chloride is rapid not only on the ^1H NMR time scale but also on the ^{119}Sn NMR time scale, and with decrease in the temperature of the solution there is only a slight broadening of the ^1H NMR signal. Unfortunately, the concentrations of the compounds studied were not reported [127], so that the results cannot be compared with earlier [123] and later (X = Cl, $Y = SC_6H_5$) [140,141] data.

A study of the regular features of the exchange reaction (12) for $R_nM = (CH_3)_3Sn$, X = Cl, and $Y = SC_6H_5$ [141] gave additional information on the mechanism of exchange reactions involving organotin halides. When the reaction was carried out in toluene, the "inverse" temperature dependence of the rate of exchange was observed, and the activation energy had a negative value (−2.3 kcal mole^{-1}). The calculated orders of the reaction (2.8 with respect to $(CH_3)_3SnCl$ and 1.0 with respect to $(CH_3)_3SnSC_6H_5$) do not depend significantly on temperature; the entropy of activation of the process has a high negative value (−62.0 kcal mole^{-1} K^{-1}). These results indicated that in relatively inert media the reaction takes place by an associative mechanism with the intermediate formation of cyclic transition states:



(IX) (X)

Since the decisive factor determining the characteristic features of the associative mechanism of exchange is the ability of the compounds R_3SnX to undergo association in inert media, a cardinal change might be expected when the reaction is studied in solvating solvents. In this case the elementary act of the reaction may involve solvated organotin molecules:



(XI)

These considerations explain the sharp increase in the rate of the exchange reaction (12) ($R_nM = (CH_3)_3Sn$, X = Cl, and Y = I) in pyridine [125], for which the transition state (XX) was proposed.

The mechanism of the exchange (12) may be even more complex in solvents of medium solvating power. In this case the equilibrium $R_3SnX + B \rightleftharpoons R_3SnX.B$ may not be displaced very far to the right, and the elementary act may involve both solvated and non-solvated molecules. This apparently explains the two-stage character of the changes observed on going from toluene to tetrahydrofuran for the exchange reaction (12) with X = Cl and $Y = SC_6H_5$ ($R_nM = (CH_3)_3Sn$); in THF the rate of the reaction decreases below −30° and increases at higher temperatures [140].

The associative mechanism has been assumed to be the most probable mechanism of the exchange reaction (12) for organotin compounds [124,125]. Two recent papers [126,128] dealing with exchange reactions (12) ($R_nM = (CH_3)_3Sn$; X, Y = Hal, X ≠ Y) explain the results by assuming a dissociative mechanism, including preliminary dissociation of the organotin halide and subsequent attack by the halide anion on an undissociated molecule:

$$(CH_3)_3SnX \rightleftarrows (CH_3)_3Sn^+ + X^-$$
$$(CH_3)_3SnY + X^- \rightleftarrows (CH_3)_3SnX + Y^- \ . \quad (15)$$

Reaction (12) has been studied in toluene [126]. Unfortunately, a detailed kinetic analysis was not carried out, and the conclusion that mechanism (15) is preferred is based only on the fact that when small quantities (~ 2×10^{-4} M) of molecular iodine are added to the solutions being studied a decrease in the rate of exchange is observed, and the pseudo-first-order rate constant is linearly dependent on $[I_2]^{-1/2}$. It is assumed [126] that molecular iodine binds the halide ions formed on dissociation (15), thus decreasing

§As already noted, a similar phenomenon was observed [108] in a study of exchange reactions in the compounds $(R_2TlOR')_2$.

their effective concentration in the solution and hence lowering the rate of the exchange reaction (the greater inhibiting action of I_2 on the exchanging systems containing $(CH_3)_3SnI$, in the authors' opinion [126], agrees with the increase in the stability constants of the ionic complexes $[I_2X]^-$ in the order $I_3^- > I_2Br^- > I_2Cl^-$).

Ladd and Glasberg [128], who studied reaction (12) in chloroform and methylene chloride, favour the ionic mechanism on the basis of the fact that with increase in the polarity of the medium there is an increase in the pseudo-first-order rate constant. In their opinion, within the framework of the associative mechanism of exchange, change in the polarity of the medium should not have such a marked influence. Various thermodynamic characteristics of this reaction have also been determined [128]. In particular, it has been shown that the exchange has a large negative entropy of activation and fairly low activation energies. Moreover, the quantity τ_A^{-1} is linearly dependent on the square of the concentration of the components of the reaction. This last fact was interpreted as indicating that the exchange is of second order not only in the cases which they studied but also for system (12) for X = Cl and Y = I; the overall order of this reaction was found to be three [125].

It may be suggested, however, that the discrepancy in the conclusions in Refs. 124, 125 and Refs. 126, 128 is due to misunderstanding and is related to the fact that the authors of Refs. 126 and 128 used pseudo-first-order rate constants in the kinetic calculations. Simple analysis¶ shows that detection of a linear relationship between τ_A^{-1} and $[A]^2$ by NMR spectroscopy unavoidably leads to the conclusion that the reaction being studied is of third order, as confirmed experimentally [125].

Proceeding to the discussion of the observations [136,138] used as arguments in support of the ionic mechanism of the exchange reactions (12), it should be noted that these observations also agree with an associative mechanism for these reactions. Thus for example the reason for the inhibiting action of small quantities of molecular iodine may be that the I_2 molecules, by coordinating to the organotin halides, prevent the formation of associates of type (IX) and (X). As far as the influence of large quantities of molecular iodine are concerned, they will act as ordinary basic additives.

The observed [128] effect of increase in the exchange rate in the study of the reaction in more polar media, within the framework of the associative mechanism, can be attributed to an increase in the polarity of the Sn–X bond. In this case there is an increase in the electrophilic character of the metal atom and the nucleophilic character of the anionic residue and hence an increase in the ability of the molecules of the organometallic halide to form associates (IX) and (X). Thus the apparent rate of exchange should increase in polar media. It should be emphasised that the suggested [126] ionisation of organotin halides is unlikely in inert media. Finally, the ionic mechanism does not explain either the high and non-integral orders observed in a number of cases for the reaction being considered or the inverse temperature dependence of the apparent reaction rate [124,141].

Thus the available facts indicate that an associative mechanism is more probable for reaction (12) for organotin compounds. It is clear, however, that more rigorous confirmation of this suggestion requires additional studies, in particular for the case where the anionic residues X and Y are halogens.

IV. C,E-EXCHANGE OF ORGANOMETALLIC GROUPS

A number of papers describe the study of the exchange of organometallic groups between anionic residues, including both carbon (R) and heteroatom groups [19,37,143,144]:

$$R_nM^*-R' + R_nM-X \rightleftarrows R_nM^*-X + R_nM-R' \quad (16)$$

Thus the ^1H NMR spectrum of an equimolar mixture of diphenylmercury and phenylmercury bromide (R = R′ = C_6H_5, M = Hg, X = Br) in dimethyl sulphoxide [143] even at 34° shows broadening of the signals of the *ortho*- and *meta*-protons corresponding to both compounds, and also of the signals due to vicinal $^{199}Hg-C-C-^1H$ spin–spin coupling. Since this effect is not observed in the study of either of these compounds individually, it was concluded that it is due to fairly intensive C,Br-exchange of phenylmercury groups in the solution.

In a number of organocadmium compounds, reactions of type (16) can be assumed on the basis of familiar results of the study of two types of compound—aryl and methyl. In particular, data on reaction (16) were obtained [144] by ^{19}F NMR for perfluoroaryl derivatives of Cd (R = R′ = C_6F_5, X = I). The study of this reaction in various solvating solvents (DMSO, DMF, etc.) showed that its rate depends on the nature of the medium.

In connection with the discovery that the rate of exchange of methyl groups in dimethylcadmium is increased catalytic quantities of CH_3CdOCH_3 and in general CH_3CdOR'',[19] reaction (16) for R = R′ = CH_3 and X = OR″ was studied by ^1H NMR [19,37]. It was found, however, that the mechanism is extremely complex and that the tetrameric molecules CH_3CdOR'' [145] exert practically no catalytic influence†. It was suggested [19,37] that this exchange process is catalysed not by tetrameric CH_3CdOR'' molecules but by small quantities of dimeric or monomeric molecules. The rate of the process in the presence of added CH_3CdOR'' increases in the order [37]: C_6H_5O, C_2H_5O > CH_3O > iso-C_3H_7O.

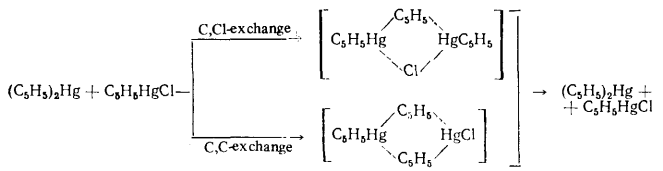
The problem of the dual character of the possible reaction mechanism also arises in the analysis of the NMR spectroscopic data obtained [35] for cyclopentadienyl derivatives of mercury. The data [35] indicated that in a mixture of the compounds $(C_5H_5)_2Hg$ and C_5H_5HgCl there is intensive intermolecular exchange. In view of the familiar lability

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¶ The rate of an exchange reaction involving both molecules of reagent A and molecules of reagent B is given by the equation: $d[A]/dt = k[A]^n[B]^m$. The lifetime of the exchanging particle in position A (τ_A) in turn is related to the reaction rate by the expression [142]: $d[A]/dt = \tau_A^{-1}[A]$. Thus $\tau_A^{-1} = k[A]^{n-1}[B]^m$. Similarly, for τ_B: $\tau_B^{-1} = k[A]^n[B]^{m-1}$. Thus the experimental determination of the values of τ_A and τ_B for different values of [A] and [B] makes it possible to find the values of m and n. For the case where [A] = [B], it is possible to determine only the overall order of the reaction $m + n$: $\tau_A^{-1} = k[A]^{m+n-1}$.

† Evidence in support of this is provided, in particular, by the detection, in the ^1H NMR spectrum of a $(CH_3)_2Cd + CH_3CdOCH_3$ mixture, of satellites of the signal of the OCH_3 group, due to $^{111/113}Cd-O-C-^1H$ vicinal spin–spin coupling [37].

of the C_5H_5Hg bond, however, there are at least two fundamentally different processes which satisfactorily explain the observed results:



In the system studied, C,Cl-exchange evidently takes place. The specific features of C_5H_5–Hg σ-bonds suggest, however, that the corresponding C,C-exchange takes place simultaneously in the system [35].

For R = CN, the exchange in mixtures (16) is of the C,E-type only from formal indications. However, since in the organic derivatives of the transition metals being considered the R_nM–CN bond is appreciably covalent, it is also appropriate to examine C,E-exchange for R = CN in this section also.

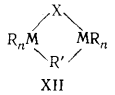
The C,E-exchange of the groups $R_nM = CH_3Hg$ [see Eqn. (16)] has been studied [104,122] for R′ = CN and X = Hal or SR″. In the case where X = Hal, the systems studied can be arranged in the following order of increasing rate of exchange with change in the halogen atom: I < Cl < Br. A study of the concentration dependence of the rate of this exchange for X = Cl [122] or SR″ [116,104] in DMF showed that the reaction is bimolecular and of first order with respect to each of the components. The reaction rate also increases sharply when DMF as solvent is replaced by pyridine [122].

Reaction (16) for $R_nM = CH_3Hg$ was also studied in aqueous solutions for R′ = CN and anionic residues X with different properties [121]. Kinetic NMR measurements showed that for X = OH (at pH > 9), Cl, SO_3^{2-}, and $S_2O_3^{2-}$, a mechanism of anion attack is possible

$$CH_3HgCN + X^{\ominus} \rightleftarrows CH_3HgX + CN^- \qquad (17)$$

whereas for exchange in the systems with X = OH (at pH < 9) and CH_3COO^-, the direct exchange reaction (16) apparently takes place.

From the data obtained, two fundamentally different routes for the exchange reaction (16) for $R_nM = CH_3Hg$ were examined [104]. The first assumes the formation of a cyclic transition state (XII) ($R_nM = CH_3Hg$, R′ = CN):



XII

whereas the second assumes that the reaction involves pre-exchange equilibria, in which ions or ion pairs separated by solvent are formed. The question of the mechanism was examined in a quantitative study [104] of exchange in system (16) ($R_nM = CH_3Hg$, R′ = CN) in DMF for a wide range of substituents X. The observed order of change in the rate of exchange:

$$Cl < OCOOH_3 < Br < SCN < SCH_3 < SC_6H_5 < SC_6H_4Cl\text{-}p < SC(CH_3)_3$$

does not coincide with the familiar order of increase in the ionic character of the bonds Hg–X (RS < CN < Br < SCN < Cl < $OCOCH_3$). Moreover, it was found that the rate constants of the exchange reactions, calculated from the ionisation constants of the compounds RHgX, are appreciably smaller than the experimental values, particularly for the case of compounds in which the Hg–S bond is highly covalent.

Thus the most probable mechanism of exchange in the compounds CH_3HgX in aprotic solvents is an associative mechanism, accompanied by the intermediate formation of cyclic transition states (XII). When both X and R′ in (XII) are substituents containing unshared pairs of electrons (Hal, SCN, SR″), the rate of exchange is too high to be observed on the NMR time scale. The replacement of one anionic group R′ by the SCN group, which is sufficiently polar but which has less tendency to coordinate to the metal atom, is accompanied by a decrease in the reaction rate constant by at least four orders of magnitude, so that the study of exchange in these systems becomes possible on the ^1H NMR time scale. When the second anionic group is replaced by the SCN group, however, the exchange reaction becomes slow on the same scale.

V. EXCHANGE BETWEEN ORGANOMETALLIC GROUPS AND A PROTON, TAKING PLACE WITH RUPTURE OF A CATIONIC PARTICLE–HETEROATOM BOND (E,E-EXCHANGE WITHIN THE FRAMEWORK OF EXCHANGE OF THE METAL–PROTON TYPE)

Among the different types of intermolecular dynamics, the least extensively studied is non-degenerate E,E-exchange, in which there is equilibrium exchange of a proton and an organometallic group:

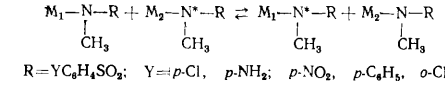
$$R_nM{-}ER'_m + H{-}E^*R'_m \rightleftarrows R_nM{-}E^*R'_m + H{-}ER'_m \ . \qquad (18)$$

Dynamics of this kind were apparently first observed by Alcock and Timms [146], when the existence of reaction (18), rapid on the PMR time scale, was assumed on the basis of an NMR study of mixtures of acetic acid and organotin or organolead acetates. It was also pointed out [146] that the replacement of phenyl groups in $R_nM = R_3Sn$ by cyclohexyl and isopropyl groups is accompanied by a decrease in the rate of exchange.

Analysis of published data shows few examples of the observation of reaction (18) by NMR. For example, the ^1H NMR spectrum of a $CH_3CdOCH_3 + HOCH_3$ mixture did not show two separate OCH_3 group signals corresponding to the individual compounds, and this result was interpreted as indicating that there is intermolecular exchange of the OCH_3 groups [37].

It should be noted that special NMR study of exchange processes of the metal–proton type in mixtures of EH-acids and their organometallic derivatives began relatively recently, and these reactions have been studied chiefly in a comparison with proton–proton reactions in EH-acids and metal–metal reactions in their organometallic derivatives.

In particular, a comparison of this kind, which made it possible to estimate the relative mobility of the hydrogen atom and organometallic groups for the case where E = N and M = Hg was carried out [10] for the case of N-methylbenzenesulphonamides and their N-phenylmercury derivatives:



$R = YC_6H_4SO_2$; Y = *p*-Cl, *p*-NH_2, *p*-NO_2, *p*-C_6H_5, *o*-Cl; (19)

a) $M_1 = M_2 = H$, proton–proton exchange;
b) $M_1 = M_2 = C_6H_5Hg$, metal–metal exchange;
c) $M_1 = H$, $M_2 = C_6H_5Hg$, metal–proton exchange.

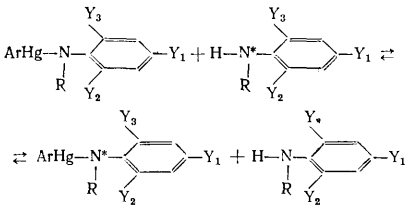
Analysis of the results showed that in a mixture of pyridine solutions of these NH-acids and their N-phenylmercury derivatives, the degenerate exchange (19a) and (19b) characteristic of the individual compounds is accompanied by another type of exchange involving the mutual

exchange of hydrogen atoms and phenylmercury groups between the same sulphonamide residues (reaction 19c). The rate of this exchange is extremely sensitive to the nature of the substituent in the benzenesulphonamide group; the rate of exchange (19c) increases in the order:

$$o\text{-Cl} < p\text{-}C_6H_5 < p\text{-}NH_2 < p\text{-}NO_2 < p\text{-Cl}\ .$$

For the system with Y = *p*-Cl it was found that this exchange is slightly slower in nitromethane than in pyridine, and much slower in chloroform than in pyridine and nitromethane. It was established[10] that under certain conditions the HgC_6H_5 group is more mobile in intermolecular exchange than the hydrogen atom.

A quantitative study of metal–proton exchange accompanied by the exchange of an arylmercury group by a hydrogen atom was carried out[116] for benzenesulphonanilides and their N-arylmercury derivatives in a pyridine–chlorobenzene (2 : 3) mixture:



(20)

R = $C_6H_5SO_2$;

a) $Y_2 = CH_3$; Ar = C_6H_5; Y_3 = H; Y_1 = H, Br, NO_2, $N(CH_3)_2$;

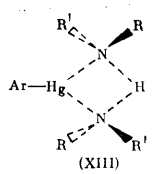
b) $Y_2 = Y_3 = CH_3$; Ar = C_6H_5; Y_1 = Br;

c) $Y_3 = CH_3$; Ar = C_6H_5; $Y_1 = Y_2$ = Br;

d) $Y_2 = CH_3$; Y_3 = H; Y_1 = Br; Ar = *p*-XC_6H_4, X = OCH_3 Cl, $N(CH_3)_2$.

The results show that the rate of reaction (20a) is increased by electron-acceptor substituents in the aryl group Y_1 on the nitrogen atom and is decreased by electron-donor substituents. At the same time, both electron-acceptor and electron-donor substituents in the arylmercury group increase the rate of this exchange process. It was shown for system (20b)[116] that reaction (20) is of first order with respect to each reagent, and its activation energy is 11.3 ± 1.3 kcal mole^{-1}. It was also demonstrated that steric hindrance, which increases on going from reaction (20a) to reaction (20b), and to a greater extent intramolecular coordination [possible on going from reaction (20b) to reaction (20c)], increase the rate of metal–metal exchange.

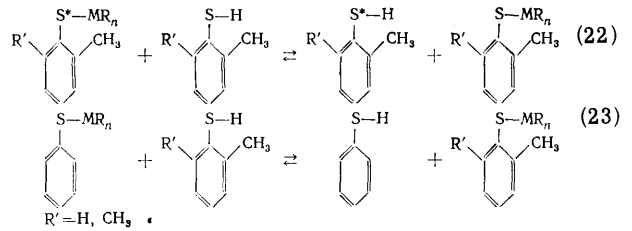
All the results indicated that the exchange reaction (19) is bimolecular and involves the intermediate formation of the cyclic transition state (**XIII**):



(XIII)

In a study of exchange between organometallic groups and a proton, accompanied by the rupture and redistribution of the bonds M–S and H–S, toluene-ω-thiol[102] or substituted thiophenols and the corresponding organometallic derivatives[102,114,115] were used as model systems:

$$C_6H_5CH_2S^*MR_n + C_6H_5CH_2SH \rightleftarrows C_6H_5CH_2S^*H + C_6H_5CH_2SMR_n \qquad (21)$$



(22)

(23)

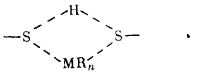
R′ = H, CH_3.

It was found that exchange (21) is slow on the NMR time scale. This feature, and also the fact that the degenerate exchange of PhHg groups in solutions of $C_6H_5CH_2SHgPh$ in chlorobenzene (8) is rapid, indicate that, as in the case of compounds containing N–H and N–Hg bonds, the PhHg group has a greater ability to undergo intermolecular exchange than the hydrogen atom.

The PMR spectra of the mixtures (22) in chlorobenzene showed[114] that metal–proton exchange is rapid only for $R_nM = SbPh_4$. In all other systems, reaction (22) is slow on the classical NMR time scale even at high temperatures. The PMR spectra of the mixtures (23) in chlorobenzene showed that the organometallic groups and the proton can be arranged in the following order of increasing ability of these cationic groups to undergo intermolecular exchange:

$$Ph_3Sn < H < Ph_3Pb \approx Ph_2Sb < PhHg < Ph_4Sb.$$

The concentration dependence of the rate of reaction (23) ($R_nM = SnPh_3$, R′ = H) showed that it is of first order with respect to each component. In addition, the steric hindrance arising on going from 2-methylthiophenol and its derivatives to 2,6-dimethylthiophenol and its derivatives decreases the rate of exchange. A study of the effect on the rate of reaction (23) of various factors which influence radical reactions (ultraviolet radiation, atmospheric oxygen, the addition of phenothiazine as inhibitor) showed fairly conclusively that this reaction does not take place by a radical mechanism. It was suggested that metal–proton exchange takes place by an associative mechanism including the formation of a cyclic transition state with delocalised bonds.



The change from solutions of systems (22) and (23) in the relatively inert chlorobenzene to solutions of the same systems in pyridine leads to an increase in the rate of metal–proton exchange (22) only in one case, namely for R′ = H, R_nM = PhHg. In all other systems, the reaction remains slow on the PMR time scale. Thus in pyridine also, the PhHg group is more mobile than the Ph_3Sn, Ph_3Pb, and Ph_2Sb groups. The effect of an increase in the rate of metal–proton exchange under the influence of pyridine in the case of other R_nM groups was shown for the case of reaction (23) (R_nM = Ph_3Sn or Ph_3Pb).

Metal–proton exchange taking place with the rupture of M–O and H–O bonds was studied for mixtures of substituted phenols and their organometallic derivatives[117]:

$$ArO^*{-}H + ArO{-}MR_n \rightleftarrows ArO^*{-}MR_n + ArO{-}H$$

Ar = 2,6-$(CH_3)_2$-4-BrC_6H_2, 2-CH_3-4-BrC_6H_3, 2-CH_3-4,6-$Br_2C_6H_2$, 2,6-$(CH_3)_2$-4-$NO_2C_6H_2$. (24)

Reaction (24) showed the following principal characteristic features at 33°: a) the PhHg group is the most mobile, and the Ph_3Sn group the least mobile in intermolecular exchange both in chloroform and in pyridine; b) increase in the

electron-acceptor properties of Ar leads to an increase in the rate of exchange; and c) the change from solutions of the corresponding systems in chloroform to solutions in pyridine also increases the rate of reaction (24).

The common features in these relationships and those previously obtained for M–N and H–N bonds on the one hand and M–S and H–S bonds on the other suggested that in the case of M–O and H–O bonds also, metal–proton exchange takes place by an associative mechanism with the formation of cyclic transition states with delocalised bonds, although additional quantitative data are required for a more detailed study of the mechanism of this reaction.

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Hydrogen Bonds and the Reactivity of Organic Compounds in Proton Transfer and Nucleophilic Substitution Reactions

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Recent data on various relations between the characteristics (spectroscopic and thermodynamic) of hydrogen bonds in different classes of organic compounds and the acid-base properties of the latter are examined. The principal approaches to the study of the influence of hydrogen bonds on acid-base equilibria in various solvents are demonstrated. Fundamentally new results, obtained in combined studies of proton transfer reactions in the gas phase and in solution, are analysed and approaches to allowance for the influence of hydrogen bonds on the reactants and the transition state in nucleophilic substitution reactions as well as the role of hydrogen bonds in the alteration of the rates and modes of chemical reactions are discussed.
The bibliography includes 152 references.

CONTENTS

I. Introduction 854
II. Hydrogen bonds and acid-base properties of organic compounds 854
III. The role of hydrogen bonds in proton transfer reactions 857
IV. Hydrogen bonds in nucleophilic substitution reactions 864

I. INTRODUCTION

Increasing attention has been devoted in recent years to problems of the dependence of the reactivity of organic compounds on the medium. Among various types of interactions contributing to the solvation energy, weak specific interactions—hydrogen bonding between the solvent and the reactants—are frequently the most important.

"During the last five years there has been a revolution in the understanding of the thermodynamics of the solvation of organic ions" [1] as a result of studies on proton transfer reactions in the gas phase in combination with quantum-chemical calculations on such reactions, whose development has been strikingly rapid. The importance of this revolution is enormous, since it leads to a change in many important postulates of theoretical organic chemistry. A comparative analysis of data on acid–base equilibria in the gas phase and in solution established that solvation factors play a much more important role than had been realised previously. For many classes of organic compounds, the influence of these factors proved to exceed in magnitude the electronic effects of substituents. The nature of the influence of substituents is in many instances different from that assumed in the study of reactions in solution. In the course of investigations the role of hydrogen bonds, which in the view of many workers determine the solvation effects, was rediscovered in a new light. In the immediate future one may expect that even more valuable information will become available and that such approaches will be extended to other types of reactions, since the growing number of studies on gas-phase reactions has an avalanche-like character.

The aim of the present review is analysis of the methodology of studies designed to discover the influence of hydrogen bonds on the equilibrium position in proton transfer reactions and on the rates, mechanisms, and modes of nucleophilic substitution reactions. From the large number of studies in which hydrogen bonds are mentioned, we therefore selected only those which provide approaches to the assessment of their role in these reactions. Acid–base equilibria are analysed in greatest detail.

II. HYDROGEN BONDS AND ACID–BASE PROPERTIES OF ORGANIC COMPOUNDS

Despite many warning signals, such concepts as acidity (basicity) and proton-donating (proton-accepting) capacity in the formation of hydrogen bonds are still treated as synonymous in the literature. The roots of this kind of confusion can be understood by comparing the following equilibria:

$$AH + B \rightleftarrows AH \ldots B \quad \text{(formation of hydrogen bonds);} \qquad (1)$$

$$AH + B \rightleftarrows A^- + HB^+ \quad \text{(acid-base equilibrium).} \qquad (2)$$

The formation of hydrogen bonds is necessary for proton transfer; it can be either an intermediate stage or it can occur in a transition state, which is assumed to consist of a hydrogen-bonded complex.

There have already been many studies (see Section III) in which possible pathways of reaction (2) have been demonstrated in relation to many examples. The overall mechanism of the interaction can be represented as follows:

$$\underset{I}{AH} + B \rightleftarrows \underset{II}{AH \ldots B} \rightleftarrows \underset{III}{A^- \ldots HB^+} \rightleftarrows \underset{IV}{A^- \ldots (S) \ldots HB^+} \rightleftarrows \underset{V}{A^- + HB^+}. \qquad (2a)$$

Here stage II involves the formation of a molecular hydrogen-bonded complex, stage III the formation of an ionic hydrogen-bonded complex or an ion pair†, stage IV the formation of a solvate-separated ion pair (S is the solvent), and stage V the dissociation into ions. Fig. 1*a* illustrated schematically the potential surface of the AH + B system, which has two minima[3]. Fig. 1*b* illustrates the dependence of the potential energy on the reaction coordinate. Curves *1* and *2* correspond to cases where either a molecular complex (the equilibrium I ⇌ II), for example,

† One should note that the term "ion pair" is a consequence of traditional usage in the literature, since complexes of a conjugate acid with an anion differ from the ion pairs formed on ion association via electrostatic forces. According to Odinokov et al.[2], such "ion pairs" resemble molecular hydrogen-bonded complexes as regards their infrared spectroscopic properties.

in a phenol–amine system, or only an ion pair (I–III), for example, in a pentachlorophenol–amine system, is formed. Curve *3* represents the situation in which both molecular and ionic complexes are in equilibrium (I⇌II⇌III), for example, in a 2,6-dichlorophenol–amine system.

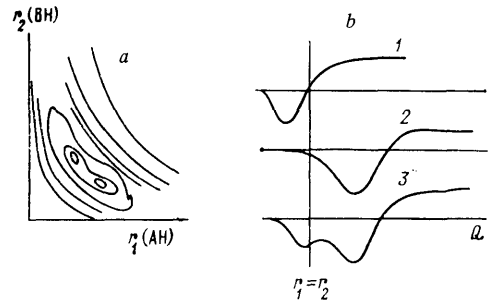


Figure 1. The potential surface of the AH + B system [3].

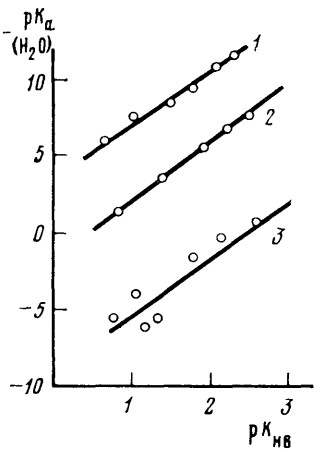


Figure 2. Relation between the free energies of protonation (pK_a) and hydrogen bond formation (pK_{HB}) reactions[10]: 1) amines; 2) pyridines; 3) carbonyl compounds.

By altering the proton-donating properties of AH, the proton-accepting properties of B, and the solvating capacity of the solvent, it is possible to drive reaction (2a) via one or other pathway. The fact that reaction (2) includes reaction (1) in some form gives rise to the idea that there is a general relation between their energetic characteristics. A relation between the linear dependence of the shifts of the stretching vibration frequencies of the AH bond [$\Delta\nu$(OH)] on formation of the hydrogen bond and the pK_a was given in an early investigation[4]. Many linear relations between frequency shifts or the hydrogen bond formation energies and the pK_a have been published in original papers[5,6] and in monographs (for example, in Ferjenson's monograph[7]). The frequency shifts $\Delta\nu$(OH) are adopted as a measure of the basicity of all solvents[8].

Convincing evidence for the absence of a single relation can be found, for example, in studies[9,10] where a thorough analysis of the relations between the free energies of reactions (1) and (2) was carried out. By analogy with pK_a, the concept of $pK_{HB} = -\lg K_{HB}$, where K_{HB} is the equilibrium constant for the formation of a hydrogen bond via reaction (1), was introduced. For all classes of compounds (aliphatic amines, pyridines, and carbonyl compounds), for which sufficient experimental data were available, three significantly linear relations, displaced along the ordinate axis (Fig. 2), were obtained. For the same capacity for the formation of hydrogen bonds (i.e. for the same pK_{HB} values), the basicity of aliphatic amines is greater by five orders of magnitude than that of substituted pyridines and by thirteen orders of magnitude that that of carbonyl compounds.

The most thorough comparative study of the hydrogen bond formation reaction (1) and the proton transfer reaction (2) was carried out by Arnett et al.[11], who analysed the ratios of the enthalpies of these reactions. The comparative analysis was based on the calorimetric method for the determination of the enthalpies of protonation (ΔH_i) in a superacid (fluorosulphonic acid) proposed previously[12]. The values of ΔH_i were compared with the calorimetric enthalpies of formation of hydrogen-bonded complexes with *p*-fluorophenol (ΔH_f). Separate linear relations are observed between ΔH_i and ΔH_f for different classes of organic compounds, similarly to data for pK_a and pK_{HB}.[10] Fig. 3 shows that the slopes of the straight lines are approximately the same.

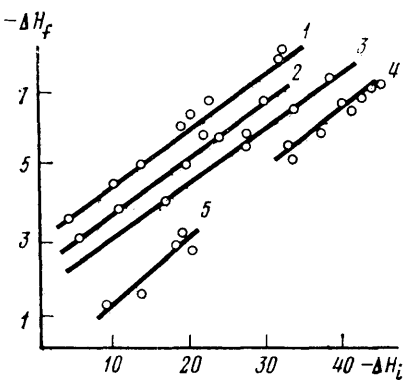


Figure 3. Relations between the enthalpies of protonation (ΔH_i) and hydrogen bond formation (ΔH_f) reactions[11]: 1) P=O; 2) S=O; 3) amides; 4) pyridines; 5) sulphides.

Studies involving such careful analyses of the relations between acid and proton donating properties of compounds of different classes have not so far been described in the literature and the amount of data permitting a comparison of the energies of different hydrogen-bonded complexes with the same base is insufficient. We therefore suggested the hydrogen-bond acidity factor (P_i), introduced[13] on the basis of the principle of the constancy of the acid and basic properties on formation of hydrogen bonds, as a characteristic of proton-donating properties.

We calculated the hydrogen-bond acidity factors from the formula

$$P_i = \Delta H_{ij}/\Delta H_{11} \cdot E_j,$$

where ΔHij is the energy of the hydrogen bond between the ith H-acid and the jth base and Ej is the basicity hydrogen-bond factor of the given base. The hydrogen-bonded complex of diethyl ether ($E_1 = 1$) and phenol ($P_1 = 1$) was chosen as the standard: $\Delta H_{11} = -5.3$ kcal mole^{-1}, i.e. the proton-donating capacity of the given acid is estimated relative to the proton-donating properties of phenol[13]. Fig. 4 clearly demonstrates the existence of different relations for different classes of compounds between the factor Pi, which we calculated from literature data[14-17], and the acidity of the compounds (alcohols, phenols, carboxylic acids, thiols). When the heteroatom in the acid AH is changed, the acid strengths of the compounds (thiols > alcohols) and their hydrogen bond proton-donating properties (thiols < alcohols) vary in opposition. The relations which obtain with retention of the heteroatom, for example, in alcohols, phenols, and carboxylic acids, can also be different (Fig. 4). Even for structurally similar "alcohols" Ph_3COH and Ph_3SiOH,[18] different relations between $\Delta\nu/\nu$ and the pK_a of the bases are observed (Fig. 5).

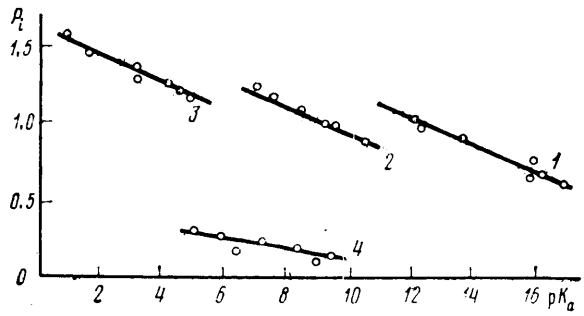


Figure 4. Relations between the acidity (pKa) and the hydrogen bond acidity factor Pi for different groups of compounds: 1) alcohols; 2) phenols; 3) carboxylic acids; 4) thiols.

Thus, as stated correctly in the review of Gur'yanova et al.[19], linear relations between thermodynamic (spectroscopic) characteristics of hydrogen bonds and acid–base properties exist only within the limits of a single class of organic compounds. The "general" relation between ΔpK_a and ΔH_{HB}, quoted by Gordi and Stanford[5], is undoubtedly erroneous and the basicity scale for solvents based on $\Delta\nu$(OH) for phenol[18] is in fact the scale of their capacity for the formation of hydrogen bonds.

The differences between the changes in the energetics of hydrogen bond formation and protonation processes for different classes of compounds are determined by many factors. In the first place, as will be shown below, the solvation energy depends significantly on the type of compound. It plays a very important role in acid–base equilibria, which had been studied previously as a rule in strongly solvating media. On the other hand, in the study of hydrogen bonds, there is a possibility of a wide-scale employment of inert solvents and in addition the influence of solvating solvents on hydrogen-bonded complexes is much smaller than on ions. Furthermore, the energetics of acid–base reactions depends on the energy of the homolytic dissociation of AH and BH^+ bonds, on the electron affinity of the A atom, and on the ionisation potential of the B atom. Proton transfer is accompanied by a significant rearrangement of the reacting molecules. The formation of hydrogen bonds does not require the dissociation of covalent bonds and a radical rearrangement of the molecule. Quantum-chemical calculations in recent years showed (see, for example, Refs. 20–23) that the changes in electron density on formation of hydrogen bonds, which are determined by charge-transfer and polarisation effects, are not restricted to a three-atom fragment including the AH bond and a heteroatom (:)B with a lone electron pair. However, these changes are much smaller than in proton transfer. At the same time, electrostatic interactions, which make the greatest contribution to the energy of hydrogen-bonded complexes according to non-empirical calculations, depend mainly on the local polarity in the region of the hydrogen bond[22], i.e. on the charges of the B and H atoms and not on the overall polarity of the reacting molecules.

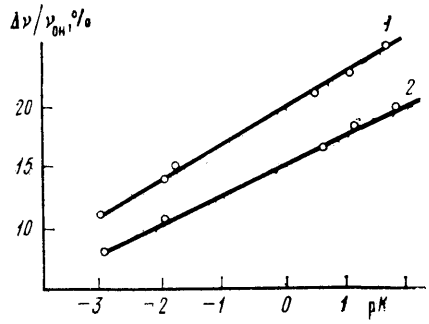


Figure 5. Relations between $\Delta\nu/\nu$ and the pK_a for Ph_3COH (line *1*) and Ph_3SiOH (line *2*).[19]

Thus, one can assume that the hydrogen bond behaves as a probe which hardly alters the given molecule during the measurement. The energy of the hydrogen bond characterises the distribution of electron density in the molecule in the ground state more adequately than does basicity or acidity.

In many instances the study of hydrogen bonds constitutes the only possibility of estimating the electron-donating properties of heteroatoms. For example, the basicity of compounds contains X–X or X–Y bonds, which are unstable when acted upon by acids (X = S, Se, or P and Y = N), cannot be determined. The study of the spectroscopic and thermodynamic characteristics of hydrogen bonds between such compounds and H-acids makes it possible to estimate their donor properties and to characterise the mutual influence of the heteroatoms[24,25]. The study of hydrogen-bonded complexes with aromatic compounds containing as a substituent a heteroatom with a lone electron pair provides a unique possibility of investigating the problem of p–π conjugation[26]. In contrast to protonation and complex formation reactions with Lewis acids, in which the n electrons of the heteroatom

constitute the reaction centre, hydrogen bonds are also formed with the aid of the π electrons of the aromatic system; infrared spectra reveal the existence of two types of hydrogen-bonded complexes [26-28]. Comparison of the spectroscopic and thermodynamic parameters of n-complexes (with a heteroatom) with the corresponding characteristics of aliphatic compounds and comparison of the parameters of π-complexes (with a π-electron system) with the characteristics of carbon analogues makes it possible to determine the redistribution of electron density on $p-\pi$ conjugation and to estimate quantitatively the degree of $p-\pi$ conjugation for different heteroatoms [25,26].

III. THE ROLE OF HYDROGEN BONDS IN PROTON TRANSFER REACTIONS

The interaction of acids and bases leading to the dissociation of acids and the protonation of bases proceeds via the formation of hydrogen bonds and ion pairs [reaction (2a)], as stated above. However, apart from this main reaction, there are a number of side reactions associated with the formation of hydrogen bonds and ion pairs with solvent molecules and the formation of hydrogen-bonded complexes between the acid (or base) and the ionic component of the anion (or conjugate acid) formed. As a result, a change in the nature of the solvent leads to a change in the thermodynamic parameters and sometimes in the relative sequence of the acidities (basicities) of various organic compounds. For this reason, investigators have endeavoured to represent thermodynamic functions as the sum of two contributions: "internal", which is independent of the influence of the medium, and "external", which is associated with the solvation of molecules [29,30]. However, the problem of the separation of these contributions and of a quantitative estimation of the role of hydrogen bonds or other types of interaction with the medium requires the development of experimental methods for the determination of the "internal" acidity (basicity), i.e. for the measurement of acid–base equilibria in the gas phase. Such data have been obtained for a wide range of organic compounds only in the last few years as a result of the development of mass-spectrometric methods.

The principal approaches to the elucidation of the influence of hydrogen bonds, obtained in the study of acid–base equilibria in solvents of different types and also when the latter were compared with the corresponding equilibria in the gas phase, are discussed below.

1. Acid–Base Equilibria in Various Solvents

Many reviews and monographs present data for the acidity and basicity constants in various solvents and the medium effects are discussed in one way or another (see, for example, Refs. 31–36). We shall consider the approaches to the isolation of the role of hydrogen bonds in proton transfer reactions.

Studies on acid–base equilibria in various media require that side reactions associated with the formation of hydrogen bonds, which are therefore different for protic and aprotic solvents, be taken into account. In view of the amphoteric nature of protic solvents, the latter exhibit two functions—those of a proton donor and acceptor. As a donor, the solvent interacts with

(a) the base:

$$SH + B \rightleftarrows SH \ldots B \rightleftarrows S^- \ldots BH^+ \rightleftarrows S^- + BH^+; \quad (3)$$

(b) with the anion formed:

$$SH + A^- \rightleftarrows SH \ldots A^- \rightleftarrows S^- \ldots HA \rightleftarrows S^- + HA. \quad (4)$$

As a proton acceptor the solvent interacts with

(a) the acid:

$$AH + SH \rightleftarrows AH \ldots SH \rightleftarrows A^- \ldots HSH^+ \rightleftarrows A^- + SH_2^+; \quad (5)$$

(b) with the conjugate acid formed:

$$BH^+ + SH \rightleftarrows BH^+ \ldots SH \rightleftarrows B + SH_2^+. \quad (6)$$

In media with a dielectric constant $\epsilon < 24$ there is a large number of ion pairs and hydrogen-bonded complexes; if $\epsilon > 24$, dissociated ions are also present [32].

Aprotic solvents can be divided into two groups: "inert", which hardly interact or only weakly interact with the reacting species (hydrocarbons and their halogeno-derivatives), and dipolar aprotic solvents, which can behave as proton acceptors [reactions (5a) and (6a) analogous to reactions (5) and (6)]:

$$AH + S \rightleftarrows AH \ldots S \rightleftarrows A^- \ldots HS^+ \rightleftarrows A^- + SH^+, \quad (5a)$$

$$BH^+ + S \rightleftarrows BH^+ \ldots S \rightleftarrows B \ldots HS^+ \rightleftarrows B + HS^+. \quad (6a)$$

In aprotic solvents of these two types reactions involving the formation of hydrogen bonds between the reactants assume a major role:

(a) between the acid and its anion:

$$AH + A^- \rightleftarrows AH \ldots A^-; \quad (7)$$

(b) between the conjugate acid and the base:

$$BH^+ + B \rightleftarrows BH^+ \ldots B. \quad (8)$$

Table 1. The equilibrium constants and the pK_a for substituted phenols–substituted pyridines and substituted phenols–triethylamine series [48].

Substituent in Ar	X	K	ΔpK_a
	$ArOH + XPy \rightleftarrows ArO^- \ldots HXPy^+$*		
2,6-Cl_2, 4-NO_2	2,4,6-Me_3	0.11	1.63
Cl_5	2,4,6-Me_3	0.15	2.17
2,6-Cl_2, 4-NO_2	3,5-Me_2	0.25	2.61
2,6-Cl_2, 4-NO_2	2,6-Me_2	0.85	3.21
2,6-Cl_2, 4-NO_2	2,4,5-Me_3	2.22	3.89
2,4,6-$(NO_2)_3$	2,4,5-Me_3	9.0	4.79
	$ArOH + NEt_3 \rightleftarrows ArO^- \ldots HNEt_3^+$**		
2,6-Cl_2	—	0.4	6.80
3,5-$(NO_2)_2$	—	0.5	6.70
2,4,6-Cl_3	—	0.9	7.03
2.4.6-Br_3	—	1.3	7.0
2,5-$(NO_2)_2$	—	2.8	5.31
Cl_5	—	2.7	5.26
2,4-$(N_2)_2$	—	6.7	4.07

* The relation between K and $\Delta pK_a = 0.7\Delta pK_a - 3.4$.
** The relation between K and pK_a is $K = -0.5pK_a + 3.5$.

In "inert" aprotic solvents acid dimers and hydrogen-bonded complexes of the acid and the base may be present together with associated species formed by reactions (7) and (8). The interaction of acids and bases in such media does not lead to dissociation into ions; it stops at the

stage involving the formation of ion pairs, which can associate into larger aggregates [36,37]. Thus the treatment of acid–base equilibria in solvents virtually lacking the capacity for specific interactions with the reactants proved to be fairly complex [31,36].

Studies devoted to the conversion of molecular hydrogen-bonded complexes into ion pairs have therefore acquired particular importance. Reliable spectroscopic criteria have been established for the identification of molecular (II) and ionic (III) hydrogen-bonded complexes in ultraviolet [38–40], infrared [2,41,42], and ^{1}H NMR spectra at low temperatures [43]. The study of the first stages of equilibrium (2a) in "inert" media made it possible to follow the changes in the nature of the interaction as a function of the proton-donating (for example, in series of halogeno- and nitro-phenols [3,38,39] and carboxylic acids [41–47]) and proton-accepting properties of the reactants (aliphatic and aromatic amines).

It has been shown [48] that there are linear relations between the equilibrium constants for the formation of ion pairs and the quantities $\Delta pK_a = pK_a(AH) - pK_a(BH^+)$ for certain series (see, for example, Table 1). In a number of studies the problem of the values of ΔpK_a for which ion pairs are formed (the II $\rightleftharpoons$ III equilibrium) [45,46,49,50] and of the differences between the enthalpies of formation of complexes II and III [2,38,44,51] has been discussed.

Much attention has been devoted to the investigation of the influence of the medium on the position of equilibrium (2). [38,48,52,53] It has been shown that the role of the solvent in the formation of ion pairs does not reduce the influence of the dielectric constant ϵ; the formation of hydrogen bonds with the solvent is of great importance, i.e. an enhancement of the proton-accepting properties of the medium shifts the equilibrium towards form III. [45,46,53]

In dipolar aprotic solvents the ion pairs $A^-...HB^+$ can be solvated specifically by the solvent with formation of solvate-separated ion pairs $A^-...(S)...HB^+$. Thus the solvation of a nitrophenol–amine complex has been investigated [54]; according to the authors, dimethyl sulphoxide is incorporated in the ion pair, forming a π-complex with the anion and hydrogen bonds with the cation: $A^-...(DMSO)...HB^+$. The molecular complex $\rightleftharpoons$ ion pair equilibrium has not been observed for oxygen-containing proton acceptors. It has been suggested that, with increase of the strength of hydrogen bonds, the evolution of complex formation proceeds from a molecular complex to an ion pair via a system in which the proton has a symmetrical position [55].

Reactions (7) and (8), occurring in dipolar aprotic solvents, have been studied by potentiometric titration and conductimetry in a series of investigations [56–60]. The formation of hydrogen bonds between the acid and the anion [reaction (7)] and between the conjugate acid and the base [reaction (8)] is referred to by the authors of the above investigations as homoconjugation processes. They showed that homoconjugation of type (7) plays a very important role; the formation constants of the complexes $(AHA)^-$ are much larger than K_{BHB^+}. [56,57,59] Enhancement of the proton-accepting properties of the solvent diminishes the homoconjugation constants. Thus the homoconjugation constants of benzoic acids in dimethylformamide (DMF) and in DMSO are smaller by a factor of 10 and 100 respectively than in acetonitrile [59].

In order to estimate the influence of homoconjugation on the proton transfer reaction, studies were made [56,57,59,60] of hydrogen bond formation reactions between the test acids AH and a model anion, for which the Cl^- anion was chosen [reaction (9)], and also between the test anion A^- and a model acid—*p*-bromophenol [reaction (10)] (the authors call these processes heteroconjugation):

$$AH + Cl^- \rightleftarrows AH \ldots Cl^-, \quad (9)$$

$$Br{-}C_6H_4OH + A^- \rightleftarrows BrC_6H_4OH \ldots A^-. \quad (10)$$

In this approach use is actually made of the principle of the constancy of acid-base functions in hydrogen bonds, already mentioned in Section II. [12,61] It has been shown in relation to benzoic acids and phenols that the sensitivity of the heteroconjugation reaction (the parameter ρ) to the electronic influence of substituents is smaller by a factor of approximately 4 than for the full proton transfer. The ratio ρ(phenol)/ρ(benzoic acid) $\simeq$ 1.8–2.0 remains constant for all the dipolar aprotic solvents employed [60].

The influence of solvents on acid–base reactions is determined overall by the operation of a large number of factors, namely (1) the formation of hydrogen bonds, (2) electrostatic interactions, (3) the basicity of (or acidity) the solvent, (4) van der Waals interactions, among which dispersion interactions are the most important, and (5) the structural organisation of the solvent. Allowance for the contributions of different factors is a complex problem, but certain approaches to its solution are available. Thus, in order to eliminate the role of electrostatic interactions, it has been suggested [62,63] that a pair of solvents of different types but with similar dielectric constants ϵ be used, namely methanol and DMF. The thermodynamic characteristics of acid–base equilibria in these two media differ greatly, demonstrating an important role of specific interactions.

Dispersion forces depend significantly on the shape and size of the interacting species, so that they must be taken into account in those cases where the equilibrium involves large highly delocalised and therefore readily polarisable anions. Such anions have a low capacity for the formation of hydrogen bonds and the role of dispersion interactions increases and may become decisive. For example, a whole class of CH acids such as derivatives of fluorene, diphenylmethane, and triphenylmethane exhibit a greater acidity in DMSO than in water, in contrast to OH acids [34,64]. In their analysis of the influence of the above factors the authors [64] note that, in solvents such as water and DMSO, factors (2) and (3) cancel out. Namely, as a result of the greater basicity of the solvent, the acidity of a given acid in DMSO should increase by 1.5 ± 0.5 pK_a units, while as a result of the lower dielectric constant ϵ it decreases by 1 pK_a unit compared with water. In the case of CH acids dispersion interactions are of greatest importance, while for OH acids the formation of hydrogen bonds is the decisive factor. The differences between the relative strengths of OH and CH acids in protic and dipolar aprotic solvents are determined by the operation of these factors. DMSO molecules, which have a larger dipole moment and polarisability than H_2O molecules, stabilise carbanions as a result of the operation of dispersion forces, which increases the acidity of CH acids in this solvent. The anions of OH acids are stabilised as a result of the formation of hydrogen bonds with water, so that their acidity in water is greater by 4–6 orders of magnitude than in DMSO.

It is noteworthy that in CH acids, whose negative charge is localised at the heteroatom (for example, benzoylacetone, nitromethane, and hydrogen cyanide), the decisive factor is the formation of hydrogen bonds with the solvent. As a result, the acidity in water is greater by 2–3 orders of magnitude than in DMSO, [34,64–66] as for OH acids. At the same time, an increase in the size of the anions of OH

acids combined with an increase of the degree of delocalisation of the charge leads to a decrease of the strength of hydrogen bonds with water and to an enhancement of dispersion forces. Thus, on passing from phenol to 4-nitro- and 2,6-dinitrophenols, the difference between the acidities in DMSO and water diminishes: the ΔpK_a values are 6.4, 3.8, and 1.3 respectively. In picric acid the sign of this quantity changes ($\Delta pK_a = -1.3$); this shows that the above acid is stronger in DMSO as a result of the stabilisation of the anion by dispersion forces [64]. A change of the sign of ΔpK_a (where ΔpK_a is the difference between the acidities in DMSO and MeOH) also takes place for 4-nitrophenol: $\Delta pK_a = 2.2$ for phenol and -0.8 for 4-nitrophenol [66].

Thus, apart from the acids giving rise to large anions with a highly delocalised charge, hydrogen bonding effects predominate over the dispersion forces and lead to a greater acidity in protic solvents.

The problems of the differentiating action of solvents, associated with their solvating capacity, have been examined in detail in a review [32] in relation to phenols and benzoic acids. It was shown that the differentiating effects of solvents can be estimated with the aid of three parameters:

(1) the autoprotolysis constant of the solvent (pK_S);

(2) the coefficient α in the equation

$$pK_{HA}(S) = \alpha pK_{HA}(H_2O) + \beta;$$

(3) the coefficient ρ in the Hammett equation:

$$pK_{HA}(S) = pK_0 - \rho\sigma.$$

Table 2. Parameters characterising the differentiating influence of solvents for monosubstituted benzoic acids [67] and phenols [32], and the solvent acidity factors in hydrogen bonds*.

Solvent	$\varepsilon_{25}°$	pK_S	α	ρ(b.a.)	ρ(ph.)	P_i
H_2O	78.5	14.0	1	1	—	0.55
CH_3OH	32.6	16.7	1.30	1.38	—	0.66
C_2H_5OH	24.3	19.5	1.60	1.66	—	0.63
C_3H_7OH	20.1	—	—	—	2.25	0.75
C_4H_9OH	17.1	—	—	—	2.59	—
iso-$(C_3H_7)OH$	18.3	—	—	—	3.17	0.75
iso-$(C_4H_9)OH$	17.7	—	—	—	2.67	0.44
$(CH_3)_2CO$	20	23.0	1.72	1.43	—	—
CH_3NO_2	36.0	24	1.81	1.83	—	—
DMF	36.7	29.4	1.98	2.03	—	—
CH_3CN	37.5	33.3	2.49	2.37	—	—
DMSO	46.6	33.3	2.49	2.57	—	—

*The parameters pK_S, α, and ρ(b.a.) for benzoic acids and ρ(ph.) for phenols are presented.

Table 2 shows that the values of pK_S, α, and ρ vary in parallel, demonstrating thereby the role of factor (3). At the same time the data in Table 2 indicate the absence of any parallelism in the variation of these parameters and the dielectric constant ϵ. Since the solvents belong to different classes of organic compounds, there need be no direct relation between their acid–base properties and their capacity for the formation of hydrogen bonds, as stated above. The role of hydrogen bonds is manifested by the fact that all the solvents which behave as proton donors exhibit smaller differentiating effects than aprotic solvents. However, Table 2 shows [32,67] that there is no direct relation between the hydrogen bond acidity factors P_i and the values of ρ. It may be that the absence of such a relation is due to the fact that the enthalpies of hydrogen-bonded complexes, from which the values of P_i were determined, had been obtained under the conditions leading to the formation of 1 : 1 complexes.

The relative activity coefficients have been used in some studies [58,68] in order to take into account the ability of solvents to form hydrogen bonds‡. The ability of a given solvent (S) to function as a proton acceptor in relation to a standard (S_0), for which acetonitrile (AN) was selected, was defined as $\lg {}^{AN}_{\gamma}{}^{S}(H_\alpha)$ with the aid of the expression

$$\lg {}^{AN}\gamma^{S}(H_\alpha) = \lg {}^{AN}\gamma^{S}(HA) - \lg {}^{AN}\gamma^{S}(MeA),$$

where HA is the acid and MeA is its methyl ester. It was assumed that the activity coefficient of the methyl ester takes into account all types of interaction other than hydrogen bonding. The activity coefficients of the acids and their esters were determined from measurements of the solubilities s:

$$\lg {}^{AN}\gamma^{S} = \lg s^{AN} - \lg s^{S}.$$

The same activity coefficients were obtained independently from differences between the heteroconjugation constants. Thus it was concluded that the quantities $\lg {}^{AN}_{\gamma}{}^{S}(H_\alpha)$ characterise the ability of the solvents to function as proton acceptors, which decreases in the following sequence:

$$DMSO\,(-1.9) > MeOH\,(-1.5) > DMF\,(-1.4).$$

The relative abilities of solvents to function as proton donors in hydrogen bonds with the anion was estimated from the values of $\lg {}^{M}_{\gamma}{}^{S}_{A^-}$, methanol (M) being selected as the standard solvent. The large negative activity coefficients obtained for dipolar aprotic solvents indicate a much higher degree of solvation of anions by methanol. The quantity $\lg {}^{M}_{\gamma}{}^{S}_{A^-}$ increases linearly with increasing basicity of the anion [68].

The activity coefficients obtained from studies on S_N2 reactions have been used [69] to estimate the influence of hydrogen bonds with the anion on the acid dissociation constant in protic solvents (H_2O, MeOH). However, one must bear in mind that this method is fairly approximate. The coefficients $\lg {}^{S_0}_{\gamma}{}^{S}_{A^-}$ for individual ions can be determined only with the aid of non-thermodynamic postulates.

Information obtained in the study of the thermodynamic characteristics of hydrogen bonds with ions by infrared spectroscopic, ^{1}H NMR, conductimetric, and calorimetric methods proved to be much more accurate and reliable (see, for example, Refs. 51 and 70–72). We believe that, in analysing the influence of solvents on acid–base equilibria, one can employ widely the enormous amount of experimental data on the thermodynamic properties of hydrogen bonds of the type AH...B (see, for example, Refs. 14 and 73). The most valuable data concerning the role of hydrogen bonds have been obtained in recent years by combining the results of studies on proton transfer reactions in the gas phase and in solutions.

‡ The relative activity coefficients $-\lg {}^{S_0}_{\gamma}{}^{S}$ reflect the change in the standard chemical potential of the solute on passing from an arbitrary standard solvent (S_0) to another solvent (S).

2. Comparison of the Parameters of the Acid–Base Equilibria in the Gas Phase and in Solution

The development of methods of ionic cyclotron resonance [74,75] and high-pressure mass spectrometry [76,77] permitted fairly accurate determinations of thermodynamic equilibria in the gas phase. The most important results in this field have been reviewed [78,79].

Proton transfer reactions of the following types were studied in the gas phase:

$$AH + B^- \rightleftarrows A^- + BH, \quad (11)$$

$$AH^+ + B \rightleftarrows A + BH^+. \quad (12)$$

If the acidity is defined as the free energy ΔG^0 of reaction (13), then the free energy of reaction (11) is a measure of the relative acidities of two acids AH and BH:

$$AH \rightleftarrows A^- + H^+. \quad (13)$$

The basicity in the gas phase is the term given to the corresponding free energy ΔG^0 of reaction (14) and ΔG^0 of reaction (12) is a measure of the relative basicities of the bases A and B:

$$BH^+ \rightleftarrows B + H^+ . \quad (14)$$

The enthalpies ΔH^0 of reactions (11)–(14) are believed to be approximately equal to the ΔG^0 in view of the smallness of the entropy effects. Special measurements of ΔS^0 of reaction (12) showed that these quantities are indeed very small [80]. The small contribution of entropy factors to reaction (11) is indicated by the insignificant changes in ΔG^0 when the temperature is altered by 300 K for a series of benzoic acids and phenols ($\Delta S^0 < 2-3$ e.u.). [81] The relative acidity or basicity [reactions (11) and (12)] are frequently designated by $\delta\Delta G^0$; the relative enthalpies are designated by $\delta\Delta H^0$.

In order to construct an absolute acidity scale [reaction (13)] or basicity scale [reaction (14)], it is necessary to calculate a thermodynamic cycle. The enthalpy change in reaction (13) caused by the proton affinity of the anion $PA(A^-)$ corresponds to the heterolytic dissociation energy and is defined as follows:

$$PA(A^-) = \Delta H^0 = DH^0(AH) - EA(A) + IP(H), \quad (15)$$

where DH^0(AH) is the homolytic dissociation energy, EA(A) electron affinity of the atom A, and IP(H) the ionisation potential of the hydrogen atom. The values of $PA(A^-)$ for a series of carboxylic acids have been determined with the aid of data for HCl and H_2S [82] and were then used as reference values in the study of benzoic acids and phenols [51].

The proton affinity of the base PA(B), corresponding to enthalpy of reaction (14), is defined in terms of the homolytic dissociation energy $DH^0(BH^+)$ and the ionisation potentials of the atoms B and H:

(16)

The internal correspondences in measurements of repeatedly overlapping thermodynamic cycles ensured an accuracy of the measurements to within 0.5 kcal mole^{-1}; the errors in the absolute values of $PA(A^-)$ and PA(B) are ±2 kcal mole^{-1}.

The existence of a linear relation between the acidities (or basicities) in the gas phase and the σ constants of the substituents has been demonstrated for certain classes of acids and bases. In all cases the sensitivity to the electronic effects of the substituents is much greater in the gas phase than in solution. Thus ρ in the gas phase is greater by a factor of 6.8 for phenols and by a factor of 10.6 for benzoic acids than in water [79,81]. According to other data [83–84], the values of ρ in the gas phase amount to 5.5–5.7 for carboxylic acids and 7.0–8.4 for alcohols; in protic solvents these quantities decrease to 1.7–1.8 and 2.7 respectively. The electronic influence of substituents on the basicity of pyridine in the gas phase is greater by a factor of 3.5 (Taagepera et al. [85]) (by a factor of 2.5, according to Arnett et al. [1]) than in water.

Table 3. The free energies and enthalpies of the reactions $XC_6H_4OH + C_6H_5O^- \rightleftharpoons XC_6H_4O^- + C_6H_5OH$ in the gas phase, water, and DMSO. [81]

X	$\Delta G^\circ_{gas} \approx \Delta H^\circ_{gas}$, kcal mole^{-1}	$\Delta G^\circ_{H_2O}$, kcal mole^{-1}	$\Delta H^\circ_{H_2O}$, kcal mole^{-1}	$\Delta G^\circ_{DMSO} \approx \Delta H^\circ_{DMSO}$, kcal mole^{-1}	$\delta\Delta H_{hydr}(A^-)$*, kcal mole^{-1}
p-OCH_3	−0.7	0.5	0.22	−0.6	−0.4
m-CH_3	0.4	0.18	0.02	0.1	−0.7
p-CH_3	1.3	0.42	0.02	1.7	−2.2
o-Cl	−6.3	−1.9	−1.1	−4.5	—
m-Cl	−7.9	−1.2	−0.3	−2.8	9.3
p-Cl	−6.6	−0.7	0.2	−1.5	10.9
p-NO_2	−25.8	−3.8	−0.8	−8.6	17.9

*$\delta\Delta H_{hydr}(A^-)$ corresponds to the difference between the heats of hydration of the anions $XC_6H_4O^-$ and $C_6H_5O^-$ on passing from the gas phase to an aqueous medium: $\delta\Delta H_{hydr}(A^-) = \Delta H_{hydr}(XC_6H_4O^-) - \Delta H_{hydr}(C_6H_5O^-)$.

Arnett et al. [1] and Mahon and Kebarle [81] claim that the main factor responsible for the weakening of the influence of substituents in protic solvents is the formation of hydrogen bonds with the anion for acids [81] and with the conjugate acid for bases [1]. Analysis of the hydration energies of the anion A^- in Table 3 on passing from the gas phase to an aqueous medium and the internal acidities of substituted phenols permits a semiquantitative characterisation of the contribution of hydrogen bonds to the change in the effect of substituents in water. Comparison of the acidities ($\Delta G^0_{gas} \simeq \Delta H^0_{gas}$) and heats of hydration of the anions [$\delta\Delta H_{hydr}(A^-)$] shows that the enhancement of the electron-accepting properties of substituents, leading to an increase of internal acidity, is almost fully compensated by the decrease of the hydration of the anion as a result of its lower basicity and ability to form hydrogen bonds§. Thus the acidity of *p*-nitrophenol increases relative to phenol by 25.8 kcal mole^{-1} in the gas phase and solvation, which stabilises the p-$NO_2C_6H_4O^-$ anion with its lower capacity for the formation of hydrogen bonds, is weakened by 17.9 kcal mole^{-1}; as a result $\Delta G^0_{H_2O}$ increases by only 3.8 kcal mole^{-1}. The decrease of the strength of $A^-\ldots(HOH)_n$ hydrogen bonds leads to an increase of the degree of disorder among solvent molecules in the vicinity of the anion, which is reflected in a greater entropy change and hence in a higher value of $\Delta G^0_{H_2O}$ compared with $\Delta H^0_{H_2O}$. Dipolar aprotic solvents, which only weakly solvate anions, have

§ As will be made clear below, the differences between the electrostatic and dispersion interactions for anions of similar size are negligible and the hydrogen bonds with the base should play a smaller role than those with the anion.

higher values of ρ (this was indicated in Section II for benzoic acids). Table 3 shows that the values of ΔG DMSO are much closer to those of ΔG gas for phenols; the attenuation factor is ~2. In contrast to the values in water, the influence of substituents is manifested in DMSO mainly by a change in enthalpy (ΔG DMSO $\simeq \Delta H$ DMSO), i.e. as in the gas phase.

The smaller the ability of the anion to form hydrogen bonds, the greater the decrease of the acidity of the corresponding acid on passing from the gas phase to water (and any other protic solvent). Thus the acidities of acetic acid and phenol are similar in the gas phase, while in water they differ by six orders of magnitude[81]. The delocalisation of the negative charge owing to the resonance effect in the phenoxide anion lowers its ability to form hydrogen bonds, which makes phenol a much weaker acid in solution. In certain classes of compounds it is necessary to take into account the stabilisation of the acids themselves in addition to the hydrogen bond with the anion. Thus benzoic acid is much stronger in the gas phase than phenol, while in water its pK_a is almost the same. This has been explained[81] by the greater ability of benzoic acid, compared with phenol, to function as a proton donor in a hydrogen bond.

The role of hydrogen bonds in the attenuation of the observed electronic influence of substituents and the change in the relative sequence of acidities in solution is manifested also by the fact that these effects are absent for acids whose anions do not possess a sufficient capacity for the formation of hydrogen-bonded complexes. Indeed, it has been shown in a series of studies[85-89] that the influence of substituents in CH acids giving rise to large ions with a delocalised charge is the same in the gas phase as in solutions; the relative acidity sequence does not change. The negligible influence of water as a solvent on the energy of proton transfer has been demonstrated for a large number of CH acids[86-88]. The differences between the basicities in the gas phase and water for aryl carbonium ions with appreciable differences in structure are constant. There is a linear relation between $\delta\Delta G_i$(gas) and $\delta\Delta G_i(H_2O)$ with a slope of unity and an intercept on the ordinate axis at ~35 kcal mole^{-1}, i.e. the enthalpy of solvation does not involve a specific interaction[87]. A satisfactory linear relation (with a slope of unity and $\rho = 1$) has been obtained [86] between the acidities of a large set of CH acids in the gas phase and in DMSO.

The most detailed study of solvation effects has been made recently[1]. The authors analysed the influence of hydrogen bonds on the acid–base equilibria of substituted pyridines and showed that the apparent weakening of the effect of substituents (by a factor of 2.5) in water can be accounted for wholly on the basis of a solvation model in which hydrogen bonds play the main role. They state that the acid–base equilibria of substituted pyridines involve an optimum reaction for this solvation model, because the ions and acid molecules have similar dimensions and shapes, so that the effects of their electrostatic and dispersion interactions are similar.

Arnett et al.[1] analysed a thermodynamic cycle and isolated the contribution of the hydrogen bonds (ΔH_{HB}) to the enthalpy of solvation (ΔH_S) calculated from heats of solution and vaporisation:

$$\begin{array}{ccc} XPyH^+_{gas} + Py_{gas} & \overset{\delta\Delta H_{i\,gas}}{\rightleftharpoons} & XPy_{gas} + PyH^+_{gas} \\ \downarrow \Delta H_S(BH^+) \quad \downarrow \Delta H_S(Py) & & \downarrow \Delta H_S(B) \quad \downarrow \Delta H_S(PyH^+) \\ XPyH^+_{H_2O} + Py_{H_2O} & \overset{\delta\Delta H_{i\,H_2O}}{\rightleftharpoons} & XPy_{H_2O} + PyH^+_{H_2O} \end{array}$$

The authors follow Krishnan and Friedman[90,91] in separating the solvation energy into (1) the enthalpy of formation of hydrogen bonds, (2) the energy of van der Waals interactions, (3) the energy of formation of a "cavity", and (4) the energy of the change in solvent structure. The last three "physical" factors were determined as an overall factor[1].

Three procedures have been used to isolate the contribution of hydrogen bonds.

1. On the basis of the principle of the constancy of the acid and basic functions in hydrogen bonds[13,61], the coefficients for the transition from *p*-fluorophenol to water as a proton donor were determined and the data of Taft et al.[10] for the p-$FC_6H_4OH\ldots XPy$ system were used.

2. The difference between the heats of solvation of substituted benzenes and pyridines was attributed to hydrogen bonds.

3. A quantum-chemical calculation was carried out on the hydrogen bond formation and proton transfer reactions.

It was shown that the experimental coefficient α ($\alpha = 0.1$) in the linear relation between the energy of formation of hydrogen bonds and the energy of proton transfer in the gas phase ΔH_{HB} ($XPy\ldots H_2O$) $= \alpha\Delta H_i$ is twice as great as the calculated value ($\alpha = 0.05$), which can be accounted for by the lower strength of the 1 : 1 hydrogen-bonded complexes, assumed in the quantum-chemical calculation, compared with the real complexes $XPy\ldots(H_2O)_n$.

The hydrogen bonds formed by charged ions play the most important role; their energy exceeds approximately by a factor of five the enthalpy of formation of hydrogen-bonded complexes of substituted pyridines¶. The influence of substituents in the $XPyH^+\ldots OH_2$ hydrogen bonds leads to the opposite relation compared with the proton transfer reaction, $\Delta H_{HB}(XPyH^+\ldots OH_2) = 0.5\Delta H_i$(gas), as for the hydrogen bonds between benzoic acids and the anions. The attenuation factor for the influence of substituents in water (2.5) can be explained satisfactorily by such variations in the strength of the hydrogen bond.

The study of Arnett et al.[1] demonstrated brilliantly the fruitfulness of this approach to the analysis of the thermodynamic cycle using the following set of data: the experimental enthalpies of proton transfer in the gas phase and in solution and the enthalpies of solvation and hydrogen bond formation in combination with the results of quantum-chemical calculations. A test of the applicability of this solvation model for hydrogen bonds to other classes of acids and bases is presumably a task for the immediate future.

The possibility of using the model for the analysis of solvation effects involving aliphatic amines is of particular interest, because the problem of the preferential contribution of electrostatic interactions or of the formation of hydrogen bonds continues to remain controversial [93-97]. Measurements of the basicities of alkylamines in the gas phase established that the anomalous basicity series in water ($NH_3 < MeNH_2 < Me_2NH > Me_3N$) is related to the solvation effects[93,96]. In the gas phase the basicity varies in accordance with expectation ($NH_3 < MeNH_2 < Me_2NH < Me_3N$). There are different linear relations between the enthalpies in the gas phase and

¶ It is of interest that comparison of the influence of hydrogen bonds formed by the pyridinium ion ($C_6H_5N^+H\ldots Cl^-$) with $MeOH\ldots Py$ showed[92] that the effect of substituents in the first case is greater by a factor of approximately 5.

aqueous solution for primary, secondary, and tertiary amines, whose slopes decrease in this sequence (Fig. 6).[93] The basicity of amines in the gas phase is 5–6 times higher than in water.

However, the interpretations of the results by Aue et al.[94] and by Arnett and coworkers[96,97] are contradictory. Aue et al.[94] believe that the irregular basicity sequence cannot be accounted for solely by the formation of hydrogen bonds of the type $BH^+ \ldots OH_2$. They claim that hydrogen bonds of this type are responsible only for the difference between the slopes of the linear plots of proton affinity against ΔH_S for primary, secondary, and tertiary amines.

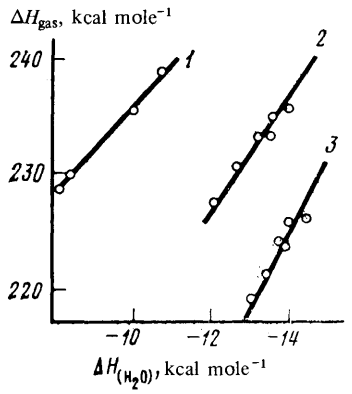


Figure 6. Relation between the enthalpies of protonation of aliphatic amines in the gas phase and water[94]: 1) tertiary amines; 2) secondary amines; 3) primary amines.

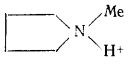
The claim by Arnett and coworkers[96,97] that hydrogen bonds are the principal differentiating factor in the solvation of ammonium ions is based on the following facts. Firstly, the solvation energy depends to a greater extent on the number of hydrogen bonds than on the size and shape of the ion. The dependences of the heat of hydration of ammonium ions on the reciprocal of the radius are different for primary, secondary, and tertiary ions, the differences increasing for large ions where the contribution of electrostatic interaction is reduced. Secondly, the average solvation energies for the three types of amines differ by 6–7 kcal mole^{-1}, which corresponds to the energies of strong $N^+H \ldots OH_2$ bonds.

Additional confirmation of the rule of hydrogen bonds was obtained on comparing the influences of substituents on the acidity of ammonium, oxonium, sulphonium, and phosphonium ions[98]. Ions of the last two types exhibit a much weaker capacity for the formation of hydrogen bonds, which means that the weakening influence of the solvent should be significantly smaller for such ions than for ammonium and oxonium ions. Indeed the influences of substituents in all four classes of compounds in the gas phase, characterised by the quantities $\Delta PA = PA(MeXH_{n-1}) - PA(XH_n)$, differ little. On the other hand, the differences between the enthalpies of protonation of methylated derivatives and hydrides in fluorosulphonic acid $[\Delta(-\Delta H)_{HSO_3F}]$ are much greater for phosphorus and sulphur derivatives than for nitrogen and oxygen derivatives. The maximum weakening of the influence of substituents in solution $[\Delta PA = 16.9$ kcal mole^{-1}; $\Delta(-\Delta H)_{HSO_3F} = 2.2$ kcal mole$^{-1}]$ is observed for oxonium ions, which corresponds to their capacity for the formation of hydrogen bonds and cannot be accounted for by electrostatic interactions. The values of ΔPA from later studies are indicated below in brackets[80,99]:

	ΔPA, kcal mole^{-1}	$\Delta(-\Delta H)_{HSO_3F}$, kcal mole^{-1}		ΔPA, kcal mole^{-1}	$\Delta(-\Delta H)_{HSO_3F}$ kcal mole^{-1}
$H_2O \rightarrow MeOH$	16,9(11,9)	2.2	$NH_3 \rightarrow MeNH_2$	11.0(9,0)	4.0
$H_2S \rightarrow MeSH$	15,0(12,0)	8.8	$PH_3 \rightarrow RPH_2$	14,4(14.4)	13.0

Comparative data on the basicities of aromatic and aliphatic amines in the gas phase and in water have been analysed in several studies[85,100–102] and several instances of the inversion of the basic strengths in solution compared with the "internal" basicity in the gas phase were noted. Thus, pyridine, which is four times less basic than ammonia in water, is eleven times more basic in the gas phase. The basicity sequence of anilines and amines in water ($Ph_3N < PhNH_2 < NH_3$) is also inverted in the gas phase: $NH_3 < PhNH_2 < Ph_3N$.[100] However, it was found that these changes are not related to the small role of resonance effects in the gas phase, but can be accounted for by the fact that the differences between the heats of solvation exceed the resonance effect in unsaturated compounds. In has been shown[85] that ΔH_S for the NH_4^+ cation is greater by 20 kcal mole^{-1} than for PyH^+, which leads to a much greater stabilisation of the ammonium ion in water. The higher heat of solvation was attributed to the greater strength of $NH_4^+ \ldots OH_2$ hydrogen bonds. However, the extent of the electrostatic interactions involving the small ion should also be greater, so that each contribution requires a special assessment.

Table 4. The heats of solution and relative acidities in the gas phase and in water of three pairs of conjugate acids differing in the degree of unsaturation[101]. The proton affinities and percentages of *s* character of the lone pair of the nitrogen atom in the corresponding amines[102].

Conjugate acid	$\Delta H_S(BH^+)$, kcal mole^{-1}	$\delta\Delta G_i$(gas), kcal mole^{-1}	$\delta\Delta G_i$(H$_2$O), kcal mole^{-1}	PA, kcal mole^{-1}	Amount of *s* character, %
	73.0	−4.3	−3.88	220.9	30
$Me_2NH_2^+$	73.0	0	0	224.6	25
	64.0	−8.3	−7.16	224.8	83
	62.0	0	0	230	25
	76.0	−9.6	−8.2	—	—
	76.0	0	0	—	—

As stated by Taft et al.[101], in order to establish the role of resonance effects one must compare the basicities of compounds with similar values of $\Delta H_S^0(BH^+)$. Such compounds are bases with the same number of acid hydrogen atoms and carbon atoms and also with a similar skeleton, differing only in the degree of unsaturation.

Under these conditions, the basicity of unsaturated compounds in the gas phase is lower than that of saturated compounds. Consequently, the resonance effect is manifested quite explicitly (Table 4) and there is no inversion in the relative basic strengths on passing from the gas phase to the solution. The changes in the basicities of unsaturated compounds are greater by 10–20% compared with saturated compounds in the gas phase relative to water, which has been explained[101] by the presence of hydrogen bonds between the bases or conjugate acids and water. The existence of a linear relation between the proton affinity and the percentage of *s* character of the lone pair orbitals of the nitrogen atom for compounds with similar values of ΔH_S has been demonstrated[102]. A greater percentage of *s* character corresponds to a lower value of *PA*, as for basicity in solution.

Marked changes on passing from the solution of the gas phase have been observed in studies devoted to the acid properties of aliphatic amines, alcohols, and thiols[103,107] (Table 5). The acidities in water decrease when the substituents are varied in the sequence Me > Et > iso-Pr > t-Bu, and there is a linear relation with the σ^* constant of the substituent. The same series, with an effective correlation between the heats of deprotonation and the σ^* constants, has been obtained in a study in DMSO.[15] However, the data in Table 5 show that in the gas phase the acidity sequence is inverted (Me < Et < iso-Pr < t-Bu), which demonstrates the lack of validity of the generally accepted relation between acidity and the inductive effect.

Table 5. The relative acidities of alcohols and thiols in the gas phase and in water ($RX^- + BuXH \rightleftharpoons BuX^- + RXH$; X = O or S).[107]

RXH	$\delta\Delta G_{gas}$, kcal mole^{-1}	$\delta\Delta G_{H_2O}$, kcal mole^{-1}	RXH	$\delta\Delta G_{gas}$, kcal mole^{-1}	$\delta\Delta G_{H_2O}$, kcal mole^{-1}
H_2O	−17.8	1.1	H_2S	1.7	5.75
MeOH	−5.6	1.7	MeSH	−4.1	1.22
EtOH	−2.7	1.0	EtSH	−1.7	0.78
iso-PrOH	−0.8	0.3	iso-PrSH	−0.8	0.49
t-BuOH	0	0	t-BuSH	0	0

The role of solvation effects has been analysed[108,109]. The enthalpies of solvation ΔH_S obtained for the anions RO^- can be arranged in the sequence $MeO^- > EtO^- >$ iso-$PrO^- >$ t-BuO^-. The values of ΔH_S then exceed the stabilisation energy of the ions in the gas phase which varies in the opposite sequence. Thus the usual ideas concerning the sign of the inductive effect, based on measurements of equilibria in solutions, are incorrect. Quantum-chemical calculations by the CNDO/2 [110] and non-empirical[111,112] methods established that, owing to its high polarisability, the alkyl group can exhibit both positive and negative inductive effects, depending on the charge on the atom to which it is linked. The calculated proton transfer energies agree with the acidities and basicities in the gas phase.

Thus measurements of the acid–base properties in the gas phase showed that solvation interactions, among which the formation of hydrogen bonds is the most important, can influence not only the magnitude but also the sequence of the properties of a series of compounds having similar structures.

We shall now consider the problem whether or not there is a general relation between acid or basic properties of organic componnds in the gas phase and the characteristics of hydrogen bonds. Strictly speaking, the comparison should be made using the characteristics of hydrogen bonds formed in the gas phase. However, the amount of data for hydrogen-bonded complexes in the gas phase is at present very small. Nevertheless, it can be shown that a general relation of this type does not exist. The lack of correspondence between the energetics of hydrogen bonds and acidity in the gas phase has been observed, for example, when the O atom in the H-acid XH was replaced by an S atom. The acidity of thiols in the gas phase is greater, as in solution, than the acidity of alcohols, while their ability to form hydrogen bonds is much weaker. This difference can be readily understood if account is taken of the fact that the energy of the acid–base equilibrium in the gas phase is an overall characteristic including the dissociation energy and the electron affinity. The lower strength of the SH bond compared with OH is the principal cause responsible for the greater acidity of thiols in the gas phase. Consequently, as one moves downwards along the Group [in the Periodic Table?] the acidity in the gas phase increases, as in solution, while the strength of hydrogen bonds with bases diminishes.

It is noteworthy that, for certain classes of compounds (aliphatic amines and pyridines), a greater similarity of the properties of hydrogen bonds and the basicities in the gas phase compared with the basicity in the solution was observed. Thus a linear relation has been obtained[113] between the energy of formation of hydrogen bonds by phenol and *p*-fluorophenol with substituted amines or pyridines and the proton affinities of these bases in the gas phase. A correlation between the basicity in the gas phase and the pK_a in water is not observed in this case, as stated previously. Studies on the frequency shifts $\Delta\nu$(OH...N) [114] and $\Delta\nu(Cl_3CH...N)$ [115] in the gas phase and the thermodynamic parameters of the $CH_3OH...N$ systems[116] in the gas phase also showed that they vary in parallel with the proton affinities in the gas phase ($Et_3N > Me_3N > Me_2NH > MeNH_2$). It is of interest to note that studies on the OH...N hydrogen bonds in solution yield other results, namely, the energies of hydrogen bonds with tertiary amines are lower than those of the bonds with secondary amines[117], i.e. there is a correlation with the basicities in solution and not in the gas phase.

Measurements on ionic equilibria of the type $(BHR^-)_{gas} \rightleftharpoons B^-_{gas} + HR_{gas}$ yielded a series corresponding to changes in the enthalpies of hydrogen bonds in parallel with the acidities of HR in the gas phase: HOH < MeOH < t-BuOH < $CHCl_3$ < PhOH < H_3CCOOH < HCOOH,[118] but it does not correspond to the energies of hydrogen bonds in solution in all respects.

We believe that there is no doubt about the importance of more extensive studies on hydrogen bonds in the gas phase and of their comparison with data for solutions and gas-phase acidities and basicities. Studies on the electron-donating and electron-accepting properties of acids and bases, extending as far as the significant rearrangement of the latter associated with the proton transfer

process, are necessary for a deeper understanding of the reactivities of compounds in acid–base reactions.

IV. HYDROGEN BONDS IN NUCLEOPHILIC SUBSTITUTION REACTIONS

The two main classes of nucleophilic substitution reactions are known to differ as regards the influence of solvents on the rate of the process:

$$Y^- + RX \begin{cases} \xrightarrow{S_{N1}} Y^- + R^+ + X^- \rightarrow YR + X^- & \text{(protic solvents accelerate the reaction),} \\ \xrightarrow{S_{N2}} [Y \ldots R \ldots X]^{\neq} \rightleftarrows YR + X^- & \text{(protic solvents retard the reaction, while aprotic dipolar solvents accelerate it).} \end{cases}$$

Unimolecular reactions are accelerated by protic solvents, since the formation of hydrogen bonds promotes the formation of the anion X^-.

The role of hydrogen bonds, which retard reactions of the S_N2 type, has been elucidated by Parker and coworkers (see, for example, Refs. 119–121). For the analysis of the influence of the solvent, use is made of the relative activity coefficients ${}^{M}_{\gamma}{}^{DMF}$, which make it possible to eliminate the influence of electrostatic interactions, since methanol (M) and DMF have similar dielectric constants, as stated previously. Examination of the results led Parker [120] to the conclusion that the main factor which determines the solvation properties of the medium is the hydrogen bonds between the protic solvent and the anion. The values of $\lg {}^{M}_{\gamma}{}^{DMF}_{Y^-}$ increase in a sequence which is the same as that corresponding to the ability of the anions to form hydrogen bonds: ClO_4^- (−0.4); 2,4,6-$NO_2C_6H_2O^-$ (−0.4) < SCN^- (2.7) < 4-$NO_2C_6H_4S^-$ (2.9) < $4NO_2C_6H_4O^-$ (4.1) < $C_6H_5S^-$ (4.9) < $C_6H_5O^-$ (7.7) < $CH_3CO_2^-$ (9.2). The delocalisation of the charge in the picrate and perchlorate anions leads to a higher degree of solvation by DMF, which is assumed to be due to the enhancement of dispersion interactions.

Analysis of the influence of the solvent made it possible to determine more effectively than by other methods the nature of the transition state. The "looser" the transition state, the greater the localisation of the negative charge, and the greater the capacity of the given substance to behave as a proton acceptor in the hydrogen bond. The quantity $\lg {}^{M}_{\gamma}{}^{DMF}_{[YR.X]^{\neq}}$ increases and the ratio of the logarithms of the rate constant $\lg k^{DMF}/\lg k^{M}$ decreases.

The change in the nucleophilicity sequence when the nature of the solvent is altered can be accounted for qualitatively from the standpoint of the ability of the solvents to form hydrogen bonds: we have $I^- > SCN^- \simeq CN^- > N_3^- \simeq Br^- > Cl^- > OAc^-$ in protic solvents [122] and $CN^- > OAc^- > Cl^- \simeq Br^- \simeq N_3^- > I^- > SCN^-$ in dipolar aprotic solvents [119]. Thus the ratio of the nucleophilicities of OAc^- and SCN^- decreases by a factor of 10^5 on passing from DMF to methanol, since the acetate ion is a much more effective proton acceptor [120].

Thus analysis of the influence of hydrogen bonds on the reaction rates assists in the study of the nature of the transition state and the prediction of the changes in the rate on replacement of the solvent. The influence of the formation of hydrogen-bonded complexes can be detected qualitatively by employing mixed solvents (see, for example, Refs. 123–126) or by analysing the changes in the rate constants which do not parallel the dielectric constants ϵ of different solvents (see, for example, Refs. 127 and 128).

For a quantitative estimate, one resorts to many-parameter equations relating the rate constant to different characteristics of the solvents (n and ϵ), including those which determine their ability to function as proton donors and acceptors (see, for example, Refs. 129–131). Thus the two-parameter expression for dipolar solvents includes the quantity $\Delta\nu_D$, which represents the shift of the stretching vibration frequency of deuteromethanol $\Delta\nu(CH_3OD \ldots B)$: [129,130]

$$\lg K_0 = -A + Bf(\varepsilon) - C(\Delta\nu_D).$$

Thus the above expression estimates the ability of the solvent to behave as a proton acceptor in the hydrogen bond [129].

Unfortunately it was found that, for a quantitative description of the effects of the medium, an equation with an even greater number of parameters is needed. Furthermore, in the case of strong specific solvation effects, the equations are inapplicable owing to the significant non-additivity of the contributions of interactions of different types [129,130].

The change from protic to dipolar aprotic solvents can also alter the mode of reaction. It has been shown in a review [132] devoted to ambident anions that, depending on the type of solvent, alkylation reactions lead to different products. The change from protic to dipolar aprotic solvents, which do not form hydrogen bonds with oxygen atoms, induces attack on the oxygen centre with formation of O-alkylation products.

Table 6. Synthesis of different products by a standard method and in the presence of KF. [135]

Product of synthesis	Reactants	t, °C	Yield, %	Time, h
$CH_3CH(O_2CPh)CO_2H$	$PhCO_2H/KF/CH_3CH(Cl)CO_2H$	130	90	0.5
ditto	$PhCO_2K/CH_3CH(Cl)CO_2H$	130	20	6
$PhO(CH_2)_4OPh$	$PhOH/KF/Br(CH_2)_4Br$	120	93	0.5
ditto	$PhOH/NaOH/Cl(CH_2)_4Cl$	150	49	1
$CH_4\langle O \rangle CH_2$	$Ph(OH_2)/KF/CH_2Br_2$	120	85	1
ditto	$Ph(OH)_2/CH_2Cl_2/NaOH(H_2O)$	110	23	15–18
$PhN(Me)CH_2N(Me)Ph$	$PhN(Me)H/KF/Cl(CH_2)_2Cl$	110	92	6
ditto	$PhN(Me)H/Na_2CO_3/Br(CH_2)_2Br$	105	83	24
$MeCH(SPh)CH_2Me$	$PhSH/KF/MeCH(I)CH_2Me$	130	92	8
ditto	$PhSNa/MeCH(Br)CH_2Me$	120	45	24

During the last two years, a series of studies by Clark and coworkers [133–136] has been published under the title "Hydrogen Bonds and Organic Synthesis". The authors showed that the formation of hydrogen bonds with KF added to the solvent greatly increases the reactivity of compounds containing the OH, NH, and SH groups in alkylation reactions. All the reactions are much faster than in the absence of KF and the yields are 80–95% (instead of 23–45%). Several examples from Clark and Miller [135] are presented in Table 6. The authors showed convincingly that KF does not participate in the reaction as a catalyst. The reactions do not rule out an initial proton transfer mechanism, because neither HF nor HF_2^- appear in solution, but hydrogen bonds are formed. Clark and Emsley [137–139] investigated the strength of the hydrogen

bonds formed by infrared spectroscopy and NMR and showed that the OH...F^- bonds are very strong (with an energy of 20–30 kcal $mole^{-1}$). It is of interest that even the much weaker NH...F^- and SH...F^- bonds also accelerate the reactions extremely effectively (by a factor of 3–4) and increase the yield by a factor of 1.5–3. In the presence of protic solvents the rate of reaction naturally decreases and the yields fall. Consequently strong hydrogen bonds can "assist" in organic synthesis, permitting the elimination of competing reactions and leading to higher yields and higher rates.

It may be hoped that the development of recently initiated studies on nucleophilic substitution reactions in the gas phase[140] will permit a quantitative assessment of the role of specific solvation, particularly the role of the formation of hydrogen bonds with the solvent.

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Thus all the facts described above show that the influence of hydrogen bonds is very great not only in proton transfer reactions but also in reactions of other types. Investigators working in the field of physical organic chemistry have sought various ways of estimating the role of hydrogen bonds, but we believe that the accumulated data on the properties and energetics of hydrogen bonds have so far been inadequately used. At the same time, within the framework of studies on hydrogen bonds, there are trends which are very important for the solution of problems associated with the reactivity of organic compounds. This concerns studies on molecular hydrogen-bonded complex–ion pair transitions, the determination of spectroscopic and energetic characteristics of ionic hydrogen bonds (between conjugate acids BH^+ and bases and between acids AH and anions), the study of the structure of the complexes $[BHB]^+$ and $[AHA]^-$, the study of hydrogen bonds in the gas phase, and the study of the influence of polar solvents on the properties of hydrogen-bonded complexes. The combination of these data is undoubtedly necessary for a deeper understanding of problems of the reactivity and structure of organic compounds.

Mention should be made of a number of studies which were published during the preparation of the manuscript for the press: on problems associated with the spectroscopic and thermodynamic characteristics of molecular hydrogen-bonded complexes and the structure of ion pairs in various solvents[141–145]; on problems concerning the elucidation of the role of hydrogen bonds by comparing the acidities and basicities in the gas phase and in solutions in different solvents[146–149]; on the problem of the influence of strong hydrogen bonds on nucleophilic substitution reactions[150–152].

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Reactions of Copper and Silver Organoacetylides

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The methods of synthesis of Group IB metal organoacetylides in weakly alkaline and neutral electron-donating media are examined and a systematic account is given of extensive experimental data concerning the reactions of copper and silver organoacetylides. Their chemical properties are compared with those of other classes of organic and organoelemental derivatives of the same metals. Much attention is devoted to the mechanisms of the reactions of copper and silver acetylides and their practical use in organic synthesis.
The bibliography includes 270 references.

CONTENTS

I.	Introduction	868
II.	Reactions involving the formation of Group IB metal organoacetylides	868
III.	Reactions of copper and silver organoacetylides with halogeno-derivatives	869
IV.	Copper and silver organoacetylides in addition reactions	886
V.	Oxidative condensation of Group IB metal organoacetylides	890
VI.	Reactions of silver organoacetylides with arenediazonium halides	890
VII.	Other reactions of copper and silver organoacetylides	891

I. INTRODUCTION

Since the publication of the first review[1] devoted to the chemistry of copper (COA) and silver (SOA) organoacetylides, this field of organometallic chemistry has greatly expanded and has been investigated in much greater depth. Copper and silver organoacetylides have been used successfully for the introduction of ethynyl groups into a wide variety of organic compounds. The heterocyclisation reaction via COA has developed greatly and heterocyclic compounds of new types have been synthesised. The ethynylation of organoelemental compounds by copper and silver organoacetylides is being used to an increasing extent. A new field of the chemistry of COA and SOA has arisen—the synthesis on their basis of ethynyl polynuclear clusters and complexes containing copper or silver together with transition metals. The synthetic scope of COA has greatly expanded with the latter used as homo- and hetero-cuprates—complexes with salts and organic derivatives of lithium, sodium, and magnesium. The COA and ethynyl cuprates have come to be used particularly frequently in the syntheses of natural products, their analogues and fragments, and physiologically active substances.

During the last ten years approximately 200 papers containing data on the structures and chemical properties of COA and SOA have been published, some of these studies having been reviewed[2-7], but the majority of the reviews are purely factual without due attention being devoted to COA and SOA from the standpoint of the characteristics of their structure and the mechanisms of their reactions.

The aim of the present review is a systematic examination and survey of extensive experimental data on COA and SOA and a discussion of the mechanisms of their reactions.

II. REACTIONS INVOLVING THE FORMATION OF GROUP IB METAL ORGANOACETYLIDES

The traditional methods for the synthesis of copper[8], silver[9], and gold[10] organoacetylides in strongly alkaline media have now been supplemented by a number of milder methods involving the use of new metallating agents, organoelemental derivatives of the acetylene series, and aprotic electron-donating solvents to which weak bases are added. These methods proved to be particularly suitable for sterically hindered or hydrolytically unstable acetylenes and acetylides as well as diacetylene compounds.

The transmetallation reaction can also be of preparative importance; copper(I) and silver(I) t-butoxides[11-13], copper(I) phenylmercaptide[14], copper(I) [15] and gold(I) [16] ketenides, as well as dry silver(I) acetate[17] have been used as metallating agents:

$$RC\equiv CH + m_i\text{-t-BuOM} \rightarrow RC\equiv CM \quad ,$$

$$M=Cu,\ R=Ph,\ SiMe_3;\ M=Ag,\ R=Ph \quad ,$$

$$PhC\equiv CH + Ph\,SCu\cdot(PPh_3)_3 \rightarrow PhC\equiv CCu\cdot PPh_3 \quad ,$$

$$PhC\equiv CH + \begin{matrix} M \\ M \end{matrix}\!\!>\!C=C=O + PhNH_2 \xrightarrow{L} PhC\equiv CM + PhNHCOMe \quad ,$$

where M = Cu and L = acetone or M = Au and L = pyridine.

The silver derivative of diazomethane also exhibits a metallating activity[18]:

$$PhC\equiv CH + \begin{matrix} Ag \\ Ag \end{matrix}\!\!>\!C=N=N \xrightarrow{\text{pyridine}} PhC\equiv CAg \quad .$$

The phosphine complexes of gold(I) organoacetylides are formed when the phosphine complexes of methylgold are acted upon by acetylenes[19,20]:

$$[AuMe(PPhR_2)] + R'C\equiv CH \xrightarrow{L} [(AuC\equiv CR')(PPhR_2)] + CH_4$$

$$R=Ph,\ R'=Ph,\ L=\text{benzene};\ R=Me,\ R'=CF_3,\ L=\text{ether}.$$

The principle of the synthesis of organocopper(I) and organosilver(I) compounds of the alkyl, vinyl, and aryl series, by treating the corresponding organoelemental derivatives with copper(I) and silver(I) salts[6], has been successfully transferred to acetylenes. Thus COA are formed almost quantitatively when tetra(arylethynyl)-borammonium is decomposed by copper(I) chloride[21,22]:

$$NH_4B(C\equiv CAr)_4 + CuCl \xrightarrow{\text{alcohol } NH_4OH} ArC\equiv CCu \quad ;$$

$$Ar=Ph;\ 2,4\text{-}Me_2C_6H_3 \quad .$$

The sterically hindered copper 2,4,6-tri-(t-butyl)-phenylacetylide was obtained in a mixture of hexane, ether,

and benzene via the mechanism[23]

$$2,4,6\text{-(t-Bu)}_3C_6H_2C\equiv CH \xrightarrow[2.\ CuI]{1.\ BuLi} 2,4,6\text{-(t-Bu)}_3C_6H_2C\equiv CCu \ .$$

This procedure is widely used nowadays for the synthesis of ethynyl organocuprates.

The synthesis of a new type of ethynyl derivatives of hexanuclear copper(I) clusters (I) is a novel application of this method[24-26]:

$$Ar_4Cu_6Cl_2 + 2LiC\equiv CR \xrightarrow[70-90\%]{\text{ether/benzene}} \underset{(I)}{Ar_4Cu_6(C\equiv CR)_2} \ ;$$

Ar=2-$Me_2NC_6H_4$; R=Ph; 4-MeC_6H_4, 2,4-$Me_2C_6H_3$, 2, 4, 6-$Me_3C_6H_2$, or $SiMe_3$.

The clusters (I) are also the products of a more complex reaction involving a transmetallation stage[25]:

$$6ArCu + 2RC\equiv CCu \xrightarrow[60\%]{\text{benzene}} (I) \ .$$

SOA can be obtained by treating Iotsich reagents with silver halides[27]:

$$BuC\equiv CMgBr + AgBr \xrightarrow[60\%]{\text{ether}} BuC\equiv CAg \ .$$

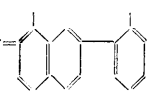
Certain representatives of organoelemental copper acetylides [compounds (II)] have been synthesised by the decomposition of ethynyl complexes of copper(I) halides in dimethyl sulphoxide (DMSO) using weak alkaline agents[28], together with dicopper(I) derivatives of diacetylene [compounds (III)][29,30], which cannot be obtained by other methods:

$$RC\equiv CH \xrightarrow[2.\ NH_4OH\ (dil.)]{1.\ CuCl,\ DMSO} \underset{(II)}{RC\equiv CCu} \ :$$

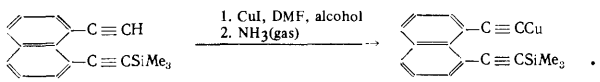
R=Bu_3P or Ph_2As

$$HC\equiv CArC\equiv CH \xrightarrow[2.\ NaHCO_3]{1.\ CuI,\ DMSO} \underset{(III)}{CuC\equiv CArC\equiv CCu} \ :$$

(a) Ar=2,2'-$C_6H_4ZC_6H_4$ (where Z=CH_2CH_2, *trans*-CH=CH, or C≡C), ;

(b) Ar=  .

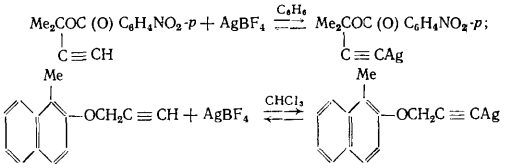
Mitchell and Sondheimer[31] obtained copper(I) arylacetylides by passing dry NH_3 for a short time through a suspension of arylacetylene and CuI in an ethanol–dimethylformamide (DMF) mixture; under these conditions, the trimethylsilyl protecting group attached to the second ethynyl group was preserved:



It has been shown[32] that copper arylacetylides are formed on heating terminal arylacetylenes and CuI in pyridine in the presence of K_2CO_3. Silver perchloroarylacetylides have been obtained by treating the corresponding acetylenes [$C_6Cl_5C\equiv CH$ and 4,4'-$(HC\equiv CC_6Cl_4)_2$] with $AgNO_3$ in a water–tetrahydrofuran (THF) mixture[33]. The oxidative disproportionation of acetylenes under the influence of copper(II) leads to COA:[11]

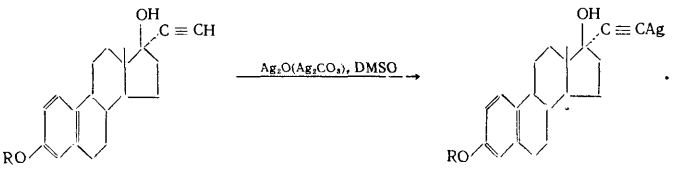
$$4PhC\equiv CH + 2Cu(OBu\text{-}t)_2 \rightarrow 2PhC\equiv CCu + (PhC\equiv C)_2 + 4\text{-t-BuOH}.$$

It has been established[34,35] that equilibrium in the system



is displaced significantly towards SOA when Ag_2CO_3 is introduced.

SOA unstable under the conditions of the synthesis are formed when 17α-ethynyl-17β-hydroxysteroids are acted upon by Ag_2O or Ag_2CO_3 in DMSO:[36]



SOA derived from disubstituted acetylenes (IV) have been obtained by the reaction of the latter with $AgNO_3$ in an aqueous or alcoholic medium[37-39]:

$$\underset{(IV)}{R_3M(C\equiv C)_nMR_3} + 2AgNO_3 \rightarrow Ag(C\equiv C)_nAg + 2R_3MNO_3 \ ;$$

n=1; M=Sn or Pb; R=Et or Ph; M=Si, R=Me or OMe; n=2 or 3; M=Pb; R=Et, C_6H_{13} or Ph .

The complex AgC≡CAg.AgCl was isolated in the decomposition of stereochemically pure *cis*- and *trans*-β-chlorovinylboronic acid with an aqueous solution of $AgNO_3$.[40]

It has been shown[41] that the complex PhC≡CH.CuCl is converted into copper phenylacetylide on treatment with solvents containing traces of water.

III. REACTIONS OF COPPER AND SILVER ORGANOACETYLIDES WITH HALOGENO-DERIVATIVES

1. Aryl and Heteroaryl Halides

A general reaction of all types of organic and heteroorganic copper(I) compounds is their condensation with aryl and heteroaryl halides in an inert atmosphere:

$$RCu + HalAr \rightarrow R\text{—}Ar + CuHal \ .$$

The compounds RCu of the first group, in which R is a powerful nucleophile [RCu = AlkCu.PR'_3, (π-C_5H_5) Cu.PR'_3, Ar_fCu, or ArC(O)OCu] [3] react in a non-ionising aprotic medium with a moderate electron-donating capacity (ether, THF, diglyme; Table 1). COA belong to the second group of the compounds RCu [where R = Alk,[43] Ar,[3] $SAlk_f$,[44,45] RS,[46] $(Me_3Si)_2N$, $(Me_3Si)_2NN(SiMe_3)$,[47] halogen[48], or CN [49]], in which the nucleophilicity of the residue R (and the amount of ionic character of the R–Cu bond) is reduced owing to coordination and possibly dative interactions of R with the copper atom. In this case the reaction medium consists of powerful electron-donating solvents (for example, DMSO, DMF, quinoline, or pyridine; see Table). 2-Methylpropenylcopper,[50] which occupies an intermediate position, approaches compounds of the first group as regards reactivity, while AlkOCu and ArOCu [51] approach compounds of the second group in this respect. The only example of the above reaction for silver(I) compounds is the condensation of perfluorophenylsilver with iodobenzene in DMF.[52]

The ethynylation of aromatic and heteroaromatic compounds with the aid of COA, first described in 1963, [53,54] is at present one of the most frequently used preparative methods in organic synthesis.

A procedure has been recently proposed for the introduction of the ethynyl group into an aromatic ring via COA, in accordance with a mechanism which does not involve their preliminary isolation[32]:

$$RC\equiv CH + IAr \xrightarrow{PyH,\ CuI,\ K_2CO_3} ArC\equiv CR \quad .$$

Table 1. The electron-donating properties and dielectric constants (ϵ) of certain aprotic solvents[42].

Solvent (D)	*Donor number* ($-\Delta H_{D,SbCl_5}$), kcal mole^{-1}	ϵ
Ether	19.2	4.3
Tetrahydrofuran	20.0	7.6
Acetone	17.0	20.7
Acetonitrile	14.1	38.0
Dimethylformamide	26.6	36.1
Dimethylacetamide	27.8	38.9
Pyridine	33.1	12.3
Hexamethylphosphoramide	38.8	30.0
Dimethyl sulphoxide	29.8	45.0
Benzonitrile	11.9	25.2
Nitrobenzene	4.4	34.8
Acetyl chloride	0.7	15.8
Benzoyl chloride	2.3	23.0

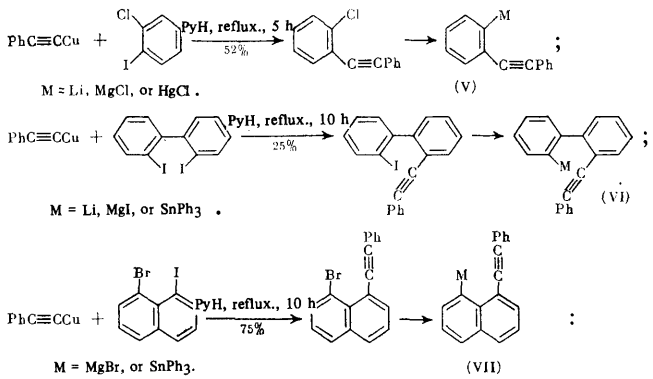
Apart from some simplification of the process, this method makes it possible to employ the complex, COA-forming terminal acetylenes which are unstable and difficult to isolate. However, one should note that successful condensation as a rule requires a large excess of CuI and of the corresponding acetylene.

In another modification of this method, used only in the synthesis of terminal arylacetylenes, a double molar excess of the acetylene compound relative to a ArI is necessary[55]:

$$(EtO)_2CHC\equiv CH \xrightarrow[2.\ CuI]{1.\ BuLi;\ hexane} \xrightarrow{PyH,\ ArI,\ 48\ h} ArC\equiv CCH(OEt)_2 \rightarrow ArC\equiv CH.$$

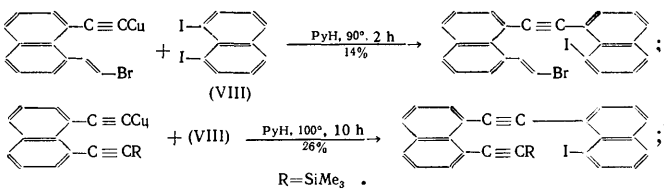
The reaction does not occur for Ar = 4-$O_2NC_6A_4$ and is facilitated in the presence of electron-donating substituents in the Ar group.

A wide variety of ethynyl derivatives of benzene, biphenyl, and naphthalene, which are the starting materials in the study of specific intramolecular electronic interactions of C≡C bonds, have been obtained by treating aryl iodides with COA. Kandil and Dessy[56] synthesised compounds (V)–(VII) with different geometrical dispositions of M and the C≡C bond:

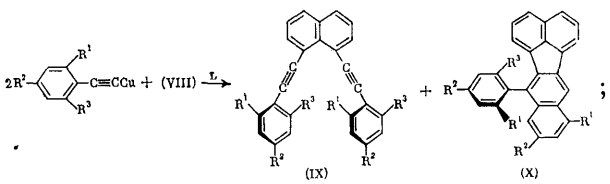


According to spectroscopic data, the metal M is not coordinated to the C≡C bond in these systems.

Interesting possibilities arise when 1,5- and particularly 1,8-di-iodonaphthalenes are used[57]. The products of the monosubstitution of 1,8-di-iodonaphthalene (VIII) have been obtained[31]:

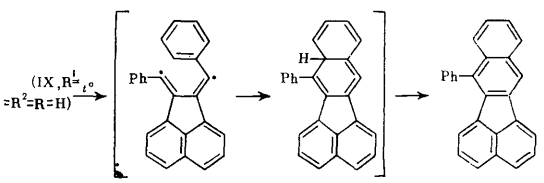


The interaction of COA with 1,8-di-iodonaphthalene has been studied in detail[58,59] and it has been shown that an increase of reaction time does not affect the overall yield of compounds (IX) and (X) (~80%), but alters sharply the (IX) : (X) ratio in favour of the latter compound if Ar = Ph and does not affect the composition of the products if Ar = mesityl [yield of (X) up to 10%] or *p*-anisyl [compound (IX) is not formed]:

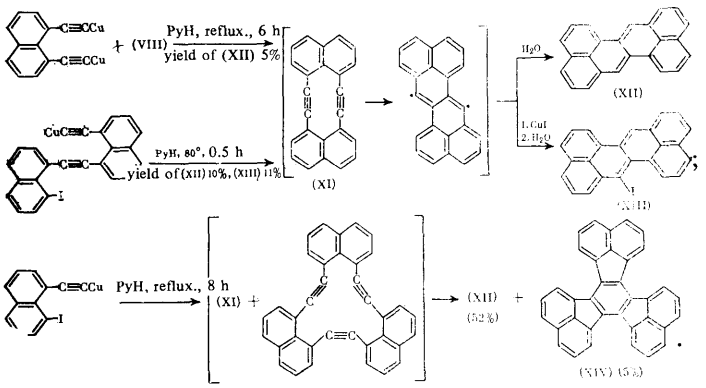


L = boiling pyridine, R^1, R^3 = H or Me; R^2 = H, Me, or OMe.

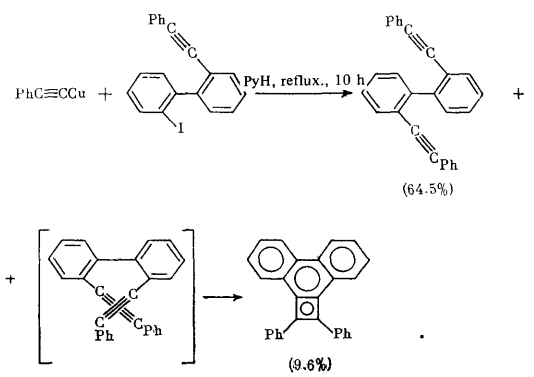
Although the system of C≡C bonds in 1,8-diethynyl derivatives of naphthalene has the non-linear *trans*-conformation[60], it is extremely reactive in intramolecular cyclisation processes, which apparently proceed via a radical mechanism. Thus it has been suggested[57] that 1,8-di(phenylethynyl)naphthalene undergoes thermal cyclisation to 7-phenylbenzo[*k*]fluoranthene via the mechanism



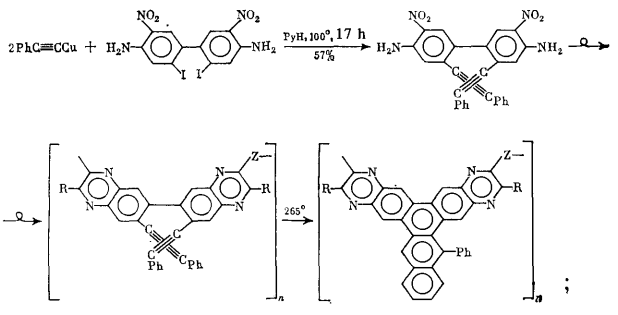
The formation of zethrene (XII), 7-iodozethrene (XIII), and decacyclene (XIV) instead to the expected dinaphthyl-1,6-bisdehydro[10]annulene (XI) [31,61] can also be readily accounted for by a radical mechanism:



It has been suggested that, when copper phenylacetylide reacts with 2-iodo-2′-phenylethynylbiphenyl, a system of crossing C≡C bonds can arise owing to rotational isomerism, in which intramolecular cyclisation takes place readily[56]

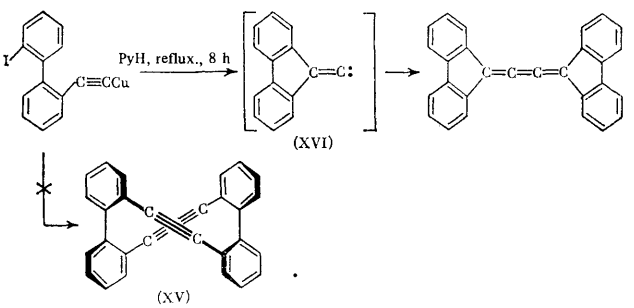


However, later it was shown[62] that the product of the cyclisation of 2,2′-di(phenylethynyl)biphenyl is 9-phenyldibenzo[*a*,*c*]anthracene, which is apparently formed by a radical mechanism analogous to that described by Bossambrock and Strechter[57]. The inclusion of such units in the polymer chain made it possible to increase significantly the thermal stability and to improve the workability of thermostable polymers. Thus the interaction of copper phenylacetylide with polyketoesters and polyesterketosulphones[63] based on 2,2′-di-iodobiphenyl-4,4′-di-carboxylic acid yielded thermally reactive binders for glass plastics [fibre glass?]. A method has been developed for the synthesis of heat-resistant polyphenylquinoxalines using 5,5′-diamino-2,2′-di(phenylethynyl)-benzidine as the tetra-amino-component[64]:

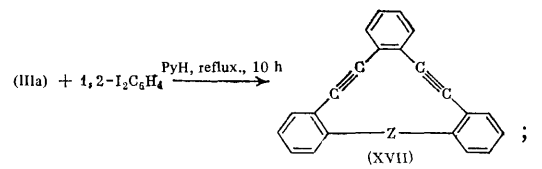


(a) R = Ph, Z = 4,4′-$C_6H_4OC_6H_4$; (b) R = 4-C_6H_4OPh, Z = 1,3-C_6H_4

At high dilutions (in pyridine) copper 2-iodo-2′-biphenylylacetylide does not form the expected homocondensation product (XV), but is converted, according to the authors[65], into di[fluorenylidene(9)]ethylene via a carbene (XVI) stage [intramolecular elimination of copper(I)]. When anaerobic conditions are not sufficiently carefully maintained, part of the initial acetylide undergoes oxidative dimerisation:

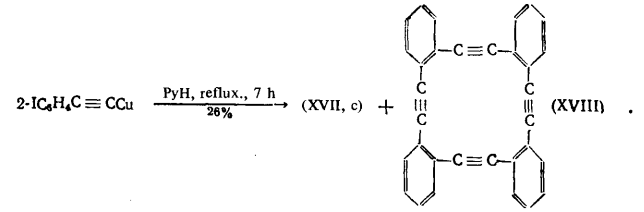


Staab and Rader[29] synthesised stable benzo[12]annulenes (XVII) by the interaction of copper(I) derivatives of diacetylenes (XIIa) with *o*-di-iodobenzene:

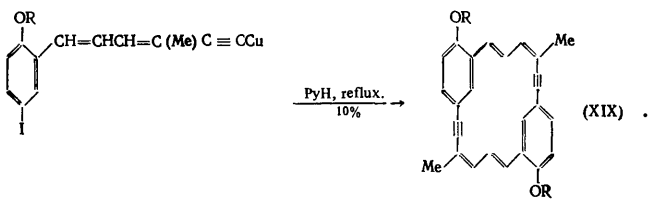


(a) Z = CH_2CH_2 (22%); (b) Z = *trans*-HC=CH (21%); (c) Z = C≡C (8%)

Previously compound (XVIIc) and the tetramer (XVIII) had been obtained by the homocondensation of copper *o*-iodophenylacetylide in pyridine[66]; structure (XVIIc) has been revised[67]:

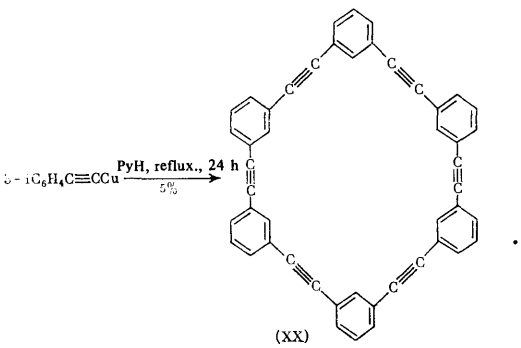


The same principle was used in the synthesis of the dehydro[18]annulenes (XIX, R = H, Me, or CH_2OMe) condensed with benzene[68]:



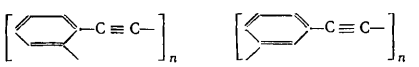
(XIX) .

We may note that, according to ultraviolet spectroscopic[67] and X-ray diffraction[69] data, there is no extended π-conjugation system in compounds (XVII, b and c). The same conclusion was also reached in relation to a 30-unit macrocyclic compound (XX) produced by the condensation of copper *m*-iodophenylacetylide[70]:



(XX)

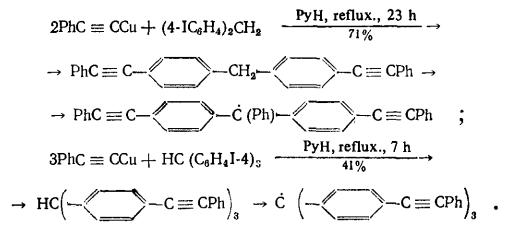
However, the main pathway in the homocondensation of copper *o*- and *m*-iodophenylacetylides in pyridine or DMF involves the formation of the open-chain polymeric systems (XXI) and (XXII) [poly(phenylene carbides)], the elementary unit of which retains the structure of the initial acetylene[71]:



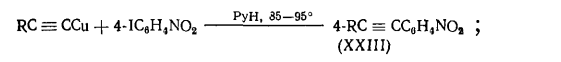
(XXI) (XXII)

The polymers (XXI) and (XXII) (M_n = 2000–10000) are distinguished by a high content of carbon (approximately 95%), are readily soluble (up to 50 wt.%) in chloroform and benzene, soften at 170°C, and are readily worked into pressed articles, fibres, and films, which, after brief heat treatment at 500°C, withstand prolonged heating without loss of weight or shape (in an inert atmosphere and even in air) at 900–1000°C. Poly(phenylene carbides) can be actively combined with many transition metal compounds via π-complex formation. Heat treatment of such compositions yields carbon-containing materials with homogeneously distributed metal particles (approximately 100 Å), which ensure protection from radiation. It has been reported[71] that the interaction of copper acetylide with di-iodobenzene isomers in pyridine or DMF also leads to poly(phenylene carbides)[71].

Diarylacetylenes have proved to be convenient for the investigation of the ability of the C≡C bond to transmit electrons. Kotlyarevskii and coworkers[72,73] used copper phenylacetylide in the synthesis of triphenylmethyl free radicals containing phenylethynyl groups:

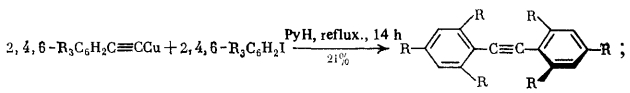


The transfer of electron density via a C≡C bond in the radical-anions (XXIII) [74] and (XXIV) [23] has also been investigated by EPR:



(XXIII)

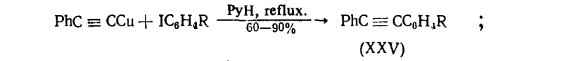
a) R = cyclopropyl (33%); b) R = Me (<1%); c) R = iso-Pr(4%).



R = t-Bu. (XXIV)

In contrast to tolanes, which do not contain bulky substituents and in which there is unhindered internal rotation of the benzene rings about the C≡C bond which leads to their preferential mutual coplanar disposition[75], di-(2,4,6-tri-t-butylphenyl)-acetylene (XXIV) constitutes a combination of two orthogonal π-systems[23].

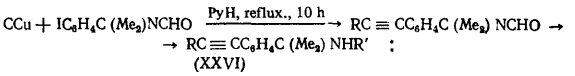
Monosubstituted tolanes (XXVa) have been synthesised for the investigation of polar and stereochemical effects in the introduction of organoaluminium groups into C≡C bonds[76]; compounds (XXVb) served as models of the products of the reaction of the phenylethynyl radical with benzene derivatives[77]:



(XXV)

(a) R = 4-Me_2N, 4-SMe, or 4-SO_2Me;
(b) R = *o*-, *m*-, or *p*-Me, Et, $CHMe_2$, CMe_3, F, Cl, or Br.

Ethynyl-substituted *N*-benzylamines, which can be readily obtained from the corresponding *N*-formyl derivatives (XXVI), proved to be effective agents for the prevention of cardiac arrhythmia[78]:



(XXVI)

a) 1,4-derivatives: R=Ph, 4'-YC_6H_4 (Y=F, Me, or OMe), 3-Py, or Bu;
b) 1,3-derivatives: R=Ph, or 3-Py .

Examples of the use of COA in the synthesis of diarylacetylenes, including derivatives with functional groups, are presented in Table 2.

Functional groups can be introduced into tolanes, which are readily available via a reaction involving COA, also in the course of subsequent treatment (see, for example, Table 3).

Table 2. The applications of COA in the synthesis of diarylacetylenes by the reaction $ArC{\equiv}CCu + IAr' \rightleftharpoons ArC{\equiv}CAr'$.

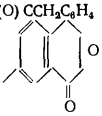
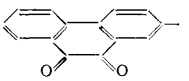
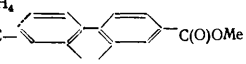
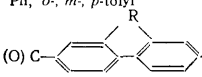
Ar	Ar'	Refs.	Ar	Ar'	Refs.
Ph	$2\text{-}C_6H_4C_6H_5$	56	Ph, $4\text{-}O_2NC_6H_4$	4-HO (O) $CCH_2C_6H_4$	81
Ph	1-naphthyl	59			
Ph	$2\text{-}H_2NC_6H_4$	8	Ph		82
$3\text{-}MeOC_6H_4$	$2\text{-}AcNC_6H_4$	79			
Ph	2-PhC (O) NHC_6H_4	8			
Ph	$2\text{-}H_2N\text{-}5\text{-}MeC_6H_3$	8			
Ph	$4\text{-}AcNHC_6H_4$	79			
Ph	$2\text{-}OHCH_2C_6H_4$	8			
$4\text{-}MeC_6H_4$	$2\text{-}Me_2NC_6H_4$	26	Ph		83
Ph	MeO (O) C—  —C(O)OMe	63			
Ph	2-MeO (O) CC_6H_4	80	$4\text{-}MeOC_6H_4$	$2\text{-}O_2N\text{-}4\text{-}MeOC_6H_3$	84
			$2,4\text{-}Me_2C_6H_3$	2, 4, $6\text{-}Me_3C_6H_2$	22
			PhC (O)	Ph; *o*-, *m*-, *p*-tolyl	85
			Ph		63
				R=4,4', 4''-$C_6H_4OC_6H_4\text{-}SO_2C_6H_4OC_6H_5$	

Table 3.

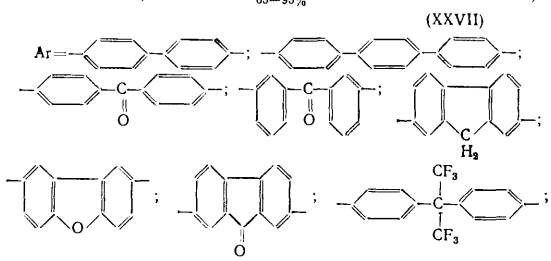
$$XC_6H_4C{\equiv}CC_6H_4Y \xrightarrow{L} X'C_6H_4C{\equiv}CC_6H_4Y'$$

X	Y	L	X'	Y'	Refs.
H	H	Anodic cyanation	H	4'-CN	86
H	H	$[PhC(O)O]_2 + I_2$, CCl_4	4-OC(O)Ph	4'-OC(O)Ph	87
$2\text{-}CH_3$	2'-CH_3	Bromosuccinimide, $[PhC(O)O]_2$, CCl_4	$2\text{-}CH_2Br$	2'-CH_2Br	67
2-Br	4'-F, Me, OMe, H	1. CuCN; 2. $LiAlH_4$	$2\text{-}CH_2NH_2$	4'-F, Me, OMe, H	78

The condensation of copper phenylacetylide with aromatic di-iodo-derivatives, previously described[8,53] in relation to di-iodobenzenes, yielded the diacetylene derivatives (XXVII), which are intermediates in the synthesis of heat-resistant and thermostable polyarylquinoxalines[64,83,88]:

$$3PhC{\equiv}CCu + IArI \xrightarrow[65-95\%]{PyH\ (DMF),\ reflux.} PhC{\equiv}CArC{\equiv}CPh\ ;$$

(XXVII)

Ar=  ;

Ethynylation in the *trans*-stilbene[29,89] and tolane[90] series has been carried out similarly:

$$2RC{\equiv}CCu + (2\text{-}IC_6H_4)_2Z \xrightarrow[60-70\%]{PyH,\ reflux.,\ 10\ h} (2\text{-}RC{\equiv}CC_6H_4)_2Z\ ;^{\dagger}$$

(a) R = *o*-tolyl, Z = *trans*-CH = CH;
(b) R = THP* $-OCH_2$, Z = *trans*-(Me)C = CH;
(c) R = Ph, Z = C≡C.

The initial configuration is largely retained in the reactions of copper vinylacetylides with aryl iodides[91-93]:

$$\underset{cis}{ROCH{=}CHC{\equiv}CCu} + IAr \xrightarrow{PyH,\ reflux.} \underset{cis}{ROCH{=}CHC{\equiv}CAr}$$

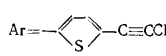
a) R=Me, Ar=$2,4\text{-}Y^1Y^2C_6H_3$ (60—90%), (Y^1=H, Y^2=H, Me, Cl, or NO_2; Y^1=NO_2, Y^2=H, or OMe); b) R=Et, or Bu, Ar=Ph (15%)

$$\underset{trans}{THPOCH_2CH{=}CHC{\equiv}CCu} + I\text{—}\langle S \rangle \xrightarrow[58\%]{PyH,\ reflux.,\ 6\ h} \underset{trans}{THPOCH_2CH{=}CHC{\equiv}C\text{—}}\langle S \rangle .$$

The formation of a mixture of *cis*- and *trans*-products by condensation in these systems[94,95]

$$\underset{trans}{MeCH{=}CH\ (C{\equiv}C)_nCu} + IAr \xrightarrow{PyH,reflux} \underset{cis,\ trans}{MeCH{=}CH\ (C{\equiv}C)_nAr}$$

(XXVIII)

a) n=1, Ar=  —$C{\equiv}CCH_2OTHP$;

(b) n=2, Ar=Ph, or 1-[^{3}H] Ph

is apparently associated merely with the instability of the *trans*-forms of compounds (XXVIII) under the reaction conditions.

The ethynylation of aromatic compounds with the aid of COA of the propargyl series is of great preparative value. Derivatives of aryl (heteroaryl) propargyl alcohols, aldehydes, and acids, which are intermediates in the synthesis of terminal aryl(heteroaryl)acetylenes, have been obtained by this method[23,96-102] (Table 4).

Arylpropargyl alcohols have been used for the chemical modification of penicillins[93] and in the synthesis of natural products of the coumarin series[102].

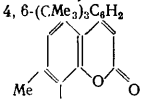
† Here and henceforth THP denotes 2-tetrahydropyranyl.

In contrast to the usual aryl iodides, the condensation of polyhalogenophenyl iodides (C_6Cl_5I, C_6Br_5I,[103] C_6F_5I,[103-104] and 4-XC_6F_4I, where X = H, F, Me, OMe, CF_3,[99] or 1,2-$I_2C_6F_4$[106,205]) with COA is complicated by transmetallation and reductive deiodination processes leading to a complex mixture of products, for example[106]:

$$2PhC\equiv CCu + 1,2\text{-}I_2C_6F_4 \xrightarrow{PyH,\ 120^\circ,\ 10\ h} 2\text{=}PhC\equiv CC_6HF_4\ (40\%) + 1,2\text{-}(PhC\equiv C)_2C_6F_4\ (25\%) + (PhC\equiv C)_2\ (20\%) + (2\text{-}C_6HF_4)_2\ (2\%)$$

Table 4.

$$RC\equiv CCu + IAr \xrightarrow{PyH} ArC\equiv CR$$

R	Ar	Refs.	R	Ar	Refs.
CH_2OH	2-thienyl	96	$CH(OMe)_2$	5-iodo-2-thienyl	101
CH_2OTHP	Ph, 1-naphthyl	97	$CH(OEt)_2$	Ph, 1-naphthyl	97
CH_2OTHP	4-$O_2NC_6H_4$, 3-Py, 4-MeO(O)CC_6H_4	98	$CH(OEt)_2$	5-X-2-thienyl (X=H, I, Me)	96, 97
CH_2OTHP	4-X-C_6F_4(X=H, F, Me, OMe, CF_3)	99	C(O)OEt	5-iodo-2-thienyl	97
CH_2OTHP	5-X-2-thienyl (X=H, I, Me)	96, 97	C(O)OEt	2, 4, 6-$(CMe_3)_3C_6H_2$	23
CH_2OTHP	3-$CF_3C_6H_4$	100	$C(Me)_2OTHP$		102

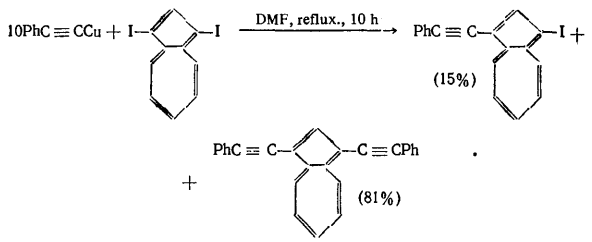
The yield of the corresponding biphenyls and 1,4-disubstituted butadiynes increases with increasing ionising capacity of the solvents (pyridine < DMF, hexamethylphosphoramide (HMP), DMSO),[99] with increase of temperature[99], and with increase of the O_2 content in the reaction mixture[103]. These factors apparently promote the exchange $RC\equiv CCu + IAr \rightleftharpoons RC\equiv CI + ArCu$, which leads to the appearance of new agents capable of condensation with the initial $RC\equiv CCu$ and ArI. In addition biphenyls and butadiynes can be formed as a result of the thermal or oxidative dimerisation of $RC\equiv CCu$ and CuAr.

Exchange processes play a major role also in the following reaction[99]:

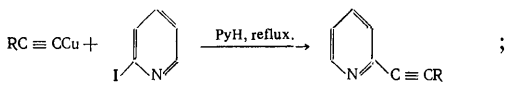
$$THPOCH_2C\equiv CCu + 4\text{-}IC_6HF_4 \xrightarrow[2.\ H^+]{1.\ PyH,\ reflux.} 4\text{-}HC_6F_4C\equiv CCH_2OH + 1,4\text{-}(OHCH_2C\equiv C)_2C_6F_4 + (4,4'\text{-}C_6HF_4)_2 + (HOCH_2C\equiv C)_2$$

COA are of great interest as agents for the ethynylation of heteroaromatic and non-benzenoid aromatic compounds. The iodo-derivatives of both electron-enriched (azulene, thiophen, and furan) and electron-deficient (compared with benzene) systems (pyridine) interact with COA much more vigorously than aryl iodides. The causes of this will be discussed when the mechanisms of the reactions of COA are considered.

Even in the presence of a large excess of copper phenylacetylide, 1,3-di-iodoazulene forms an appreciable amount of the monosubstituted product together with the disubstituted product[107]:

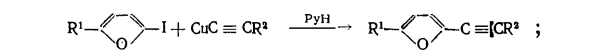


The condensation of COA with 2- and 3-iodopyridines is 5–10 times faster than the condensation with iodobenzene[8,108] and leads to high yields of pyridylacetylenes for the optimum reaction time (2 h):[108]

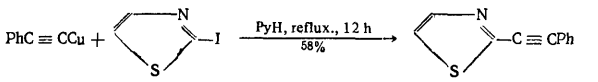


R=Ph (86%), 4-$MeOC_6H_4$ (68%), 4-$O_2NC_6H_4$ (52%), 4-PhC_6H_4 (54%), or Bu (95%)

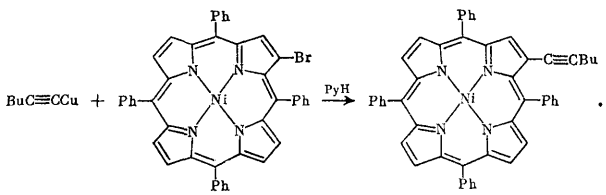
2-Iodo-derivatives of furan[96,109,110] and thiazole[110] as well as derivatives of 4-iodopyrazole[139] readily enter into a similar reaction:



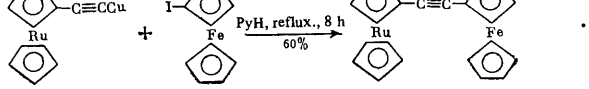
(a) R^1=H, R^2=CH_2OH, CH_2Ph, or Ph; (b) R^1=Me, R^2=CH_2OH; (c) R^1=C(O)OEt, R^2=Me; (d) R^1=CHO, or C(O)Me, R^2=Ph, or $C\equiv CPh$;



The condensation of COA with iodo-derivatives of the thiophen series has been frequently used by Bohlmann and by Atkinson, Curtis, and Taylor in the syntheses of the analogues of natural acetylenic products and their fragments (Table 5). This method provides unique possibilities for the introduction of asymmetric ethynyl groups in the 2,5-positions of the thiophen ring and the synthesis of disubstituted acetylenes containing 2-bithienyl groups. Examples of the interaction of COA with iodothiophens (the bromo-derivatives do not react) are presented below. The bromo-derivative of the Ni-tetraphenylporphyrin system is fairly reactive in relation to COA:[118]



Iodoferrocenes condense smoothly with COA, forming substituted ferrocenylacetylenes[111,119,120]:



As in the case of the mono iodo-derivative, copper ferrocenylacetylide reacts much more vigorously with 1,1-diiodoferrocene than does copper phenylacetylide[120]. The homocondensation of copper 1-ferrocenyl-1-iodoacetylide

yielded 2,2-ferrocenophane-1,3-diyne[121]:

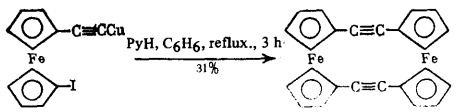
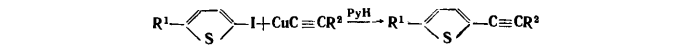
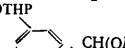
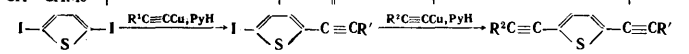


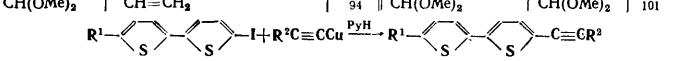
Table 5. The applications of COA in the synthesis of thienylacetylenes.



R^1	R^2	Refs.	R^1	R^2	Refs.
H	Ph, 1-ferrocenyl	111	CH_2OAc	*trans*-CH-CHCH2- -AcO OTHP	114
H	CH-CHCH$_2$OTHP	112	C≡CMe	 , $CH(OMe)_2$	115
Ph	Me	96			
C(O)Et, CH(OEt) 2, I, CH=CHMe	Me	113	CHO	Me	96



R^1	R^2	Refs.	R^1	R^2	Refs.
Me	C≡CCH=CH$_2$	94	CH_2CH_2OH	C≡CMe	94
			C≡CMe	CH=CH$_2$	94
CH_2OTHP	C≡CCH=CH$_2$, CH=CHMe	94	CH(OTHP)CH_2OAc	C≡CMe	94
$CH(OMe)_2$	CH=CH$_2$	94	$CH(OMe)_2$	$CH(OMe)_2$	101

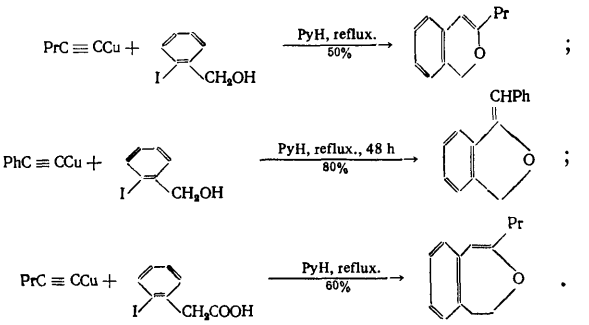


R^1	R^2	Refs.	R^1	R^2	Refs.
H	Me, CH_2OH, CH=CH$_2$, CH_2CH_2OH, C(O)Me, $CH(OE)_2$	117	Me, C(O)OMe I, C≡CCH$(OMe)_2$	CH=CH$_2$ $CH(OMe)_2$	116 117
H	CH_2OTHP	97			

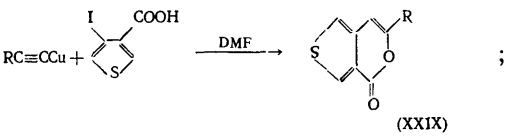
COA containing heteroaromatic substituents have been little investigated. Apart from the reactions discussed above, the condensation of copper 1-ferrocenylacetylide with 2-iodothiophen[111], 1-iodonaphthalene, and 2-iodophenol[119], of copper 2,5-dideutero-1-ferrocenylacetylide with iodobenzene[122], of copper 2-thienylacetylide with 2-iodothiophen[110], 5-formyl-2-iodothiophen, and 5-acetyl-2-iodothiophen[101], and of copper 2-pyridylacetylide with 2-iodoaniline[8] have been described.

Castro and coworkers established in early investigations[8,123] that the interaction of COA in DMF or pyridine with aryl halides containing nucleophiles Y = NH_2, SH, OH, or COOH in the *o*-position leads to heterocyclic products of the intramolecular nucleophilic addition of Y to the newly formed disubstituted C≡C bond π-linked to CuHal. In subsequent studies the range of *o*-substituted aryl halides and COA used was greatly extended, which made it possible to synthesise many heterocyclic systems which had been difficult to obtain hitherto or were completely new.

COA readily condense with *o*-iodobenzyl alcohol and *o*-iodophenylacetic acid, while the alkyl homologues of the latter form only homocyclisation products under these conditions[124]:



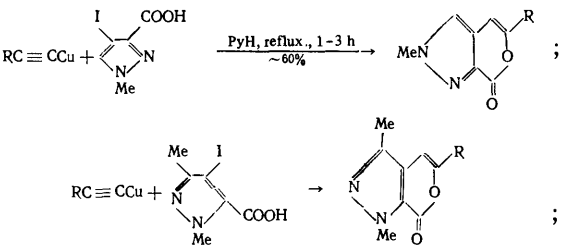
The first examples of a new class of heterocyclic compounds—substituted 1*H*-thieno[3,4-*b*]-2-alkyl(aryl)-1-pyranones (XXIX)—have been described[125]:



(XXIX)

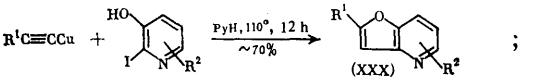
R=Pr, Bu, C_6H_{13} or Ph.

Similarly 4-iodo-*N*-methylpyrazolecarboxylic acids react with COA to form exclusively δ-lactones derived from 6-methyl-1-oxopyrano[3,4-*c*]pyrazole and 5,7-dimethyl-1-oxopyrano[3,4-d]pyrazole[126]:



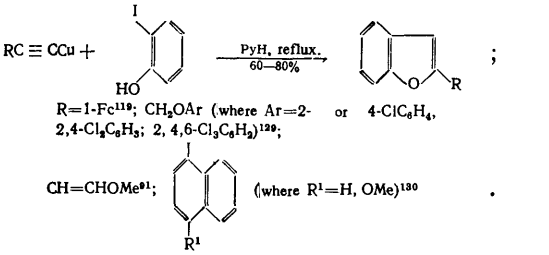
R=Ph, Pr, CH_3, or OMe.

The syntheses of condensed furan systems from *o*-iodoxyarene derivatives and COA have acquired considerable practical importance. Furo[3,2-*b*]pyridines (XXX a and b) have been obtained by this procedure for the first time[125, 127, 129]:



(a) R^1 = Pr, Bu, C_6H_{13}, CH_2CH_2OH, or Ph; R^2 = H;
(b) R^1 = Pr or Bu; R^2 = 2- or 4-Me.

Complex substituents have also been introduced into the 2-position of benzofuran with the aid of COA:



R=1-Fc[119]; CH_2OAr (where Ar=2- or 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$; 2, 4,6-$Cl_3C_6H_2$)[129];

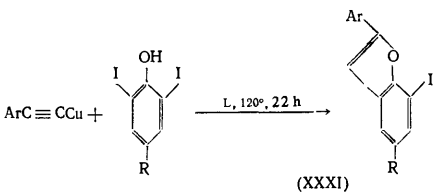
(where R^1=H, OMe)[130]

A wide variety of derivatives of this series—natural products and their analogues—have been synthesised similarly.

Table 6.

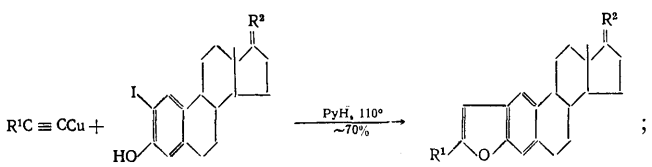
L	Ar	R	Yield of (XXXI), %
PyH	Ph	CHO	26
		$CH_2C(O)OMe$	44
		$CH_2CH(NHAc)C(O)OMe$	32
DMF	$4\text{-}MeOC_6H_4$	$CH_2C(O)OMe$	16
		$CH_2CH(NHAc)C(O)Me$	18
DMF	$4\text{-}MeO\text{-}3\text{-}iso\text{-}PrC_6H_3$	$CH_2C(O)OMe$	63
		$CH_2CH(NHAc)C(O)OMe$	40

4-Substituted 2,6-di-iodophenols react with copper phenylacetylide in pyridine and with COA whose benzene ring contains electron-donating substituents in DMF to form iodobenzofurans (XXXI), which are potential analogues of thyroxine (Table 6)[131]:



(XXXI)

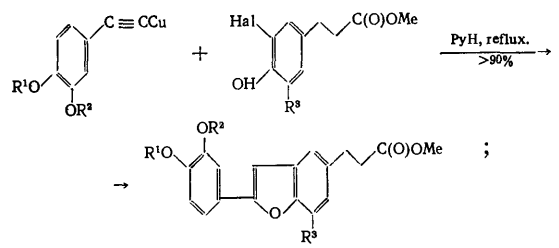
The use of COA opens a new pathway to the synthesis of heterocyclic steroids[132]:



(a) R^1=Pr, Bu, C_6H_{13}, or CH_2OH, Ph; R^2=O;
(b) R^1=Pr; R^2=



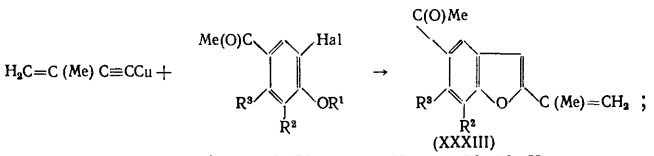
The natural "lignanes" (XXXII) are the only products of the reaction when the halogen is iodine; with bromine as the halogen, appreciable amounts of diarylbutadiynes were isolated[133]:



(XXXII)

(a) R^1 R^2=$-CH_2-$; R^3=H or OMe;
(b) R^1=R^2=Me; R^3=H or OMe.

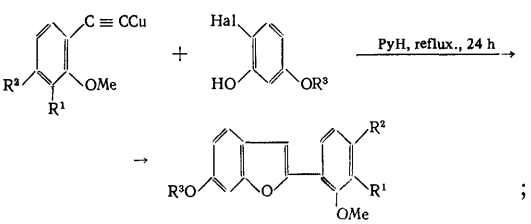
Natural products of the 5-acetyl-2-isopropenylbenzofuran series ("norlignanes") have been obtained by the condensation of copper isopropenylacetylide with 3-halogeno-4-hydroxyacetophenones in quinoline (XXXIIIa)[134] and pyridine (XXXIII, b–g).[135] Compound (XXXIIIa) is not formed if the initial phenol reacts in the free rather than acylated form[134]:



(XXXIII)

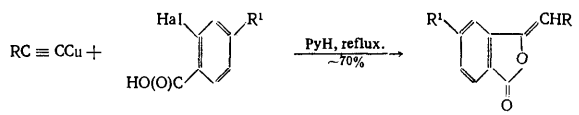
(a) Hal=Br, R^1=Ac, R^2=R^3=OAc; (b) Hal=Br, R^1=R^3=H, R^2=OH; (c) Hal=I, R^1=R^2=R^3=H;
(d) Hal=I, R^1=H, R^2=OMe, R^3=OH.

The synthesis of two natural products of the 2-arylbenzofuran series was described recently[136]:



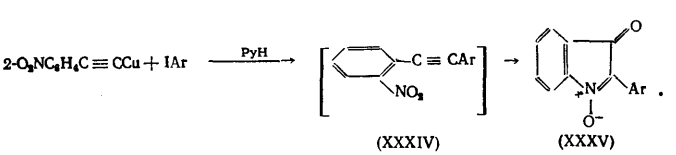
(a) R^1=OAc, R^2=OMe, R^3=CH_2Ph, Hal=I (78%);
(b) R^1=H, R^2=OCH_2Ph, R^3=Me, Hal=Br (34%)

The cyclisation reactions examined above take place unambiguously at the β-carbon atom (relative to copper), whereupon a hydrogen atom migrates from the functional group in the ring to the α-carbon atom of the ethynyl fragment of the COA. The mode of cyclisation of *o*-halogenobenzoic acids is reversed[8]: with R = n-Pr, R′ = H, and Hal = I, a mixture of 3-n-propylisocoumarin and 3-n-butylidenephthalide is formed, i.e. both cyclisation pathways operate[8]:



R=Ph; R^1=H, Cl; Hal=Cl

The key factor in the cyclocondensation of COA involving NO_2 and $C(O)NH_2$ groups is the migration of the O atom to the α-carbon atom. Thus heating of copper *o*-nitrophenylacetylide with aryl iodides in pyridine leads to 2-aryl-substituted isatogens[84] (Table 7):

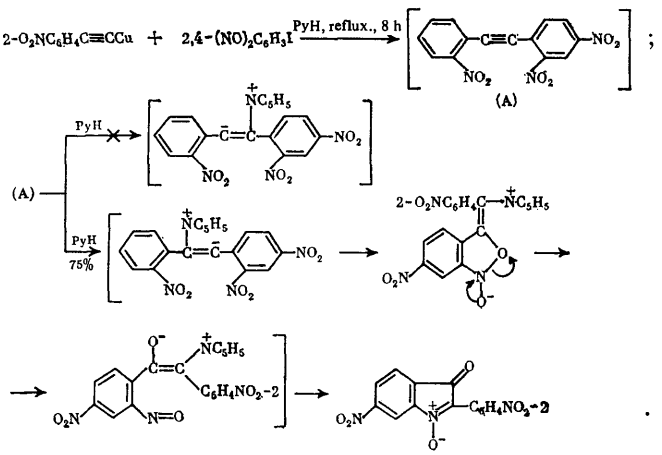


(XXXIV) (XXXV)

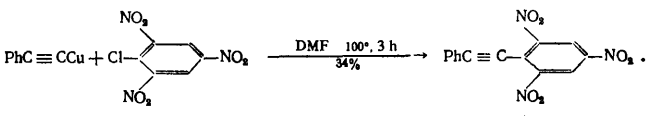
Table 7.

Ar	Yield of (XXXV), %	Ar	Yield of (XXXV), %
4-$MeOC_6H_4$	37	2-O_2N-4-$MeOC_6H_3$	66
4-$O_2NC_6H_4$	71	2-$C_6H_4C_6H_5$	73
2-O_2N-3-$MeOC_6H_3$	70	3-Py	22
		2-Thienyl	69

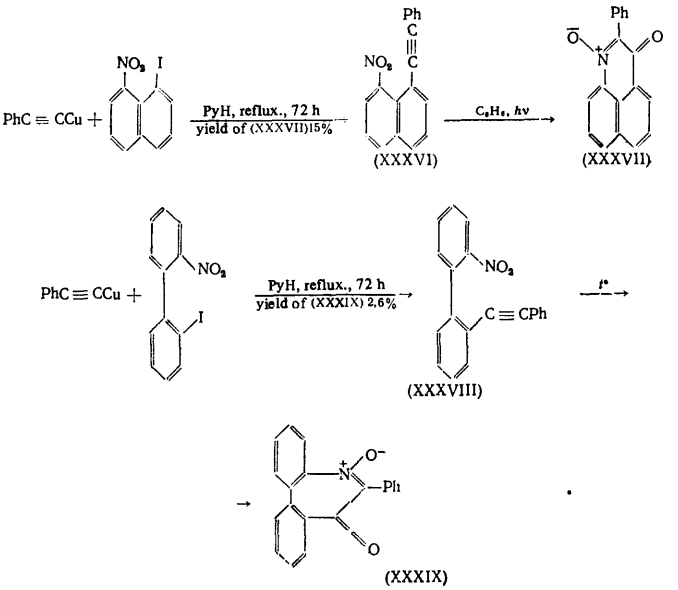
In conformity with the proposed mechanism, the cyclisation proceeds in the direction of the aromatic ring with the most pronounced electron-accepting properties:



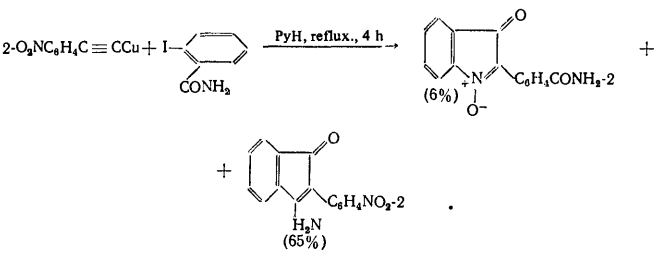
Steric factors (for example, *o*-substituents in the aryl group have a strong influence on the cyclisation. Thus the yield of (XXXIV) with Ar = 2-MeC_6H_4, 2-$MeOC_6H_4$, 2-$NO_2C_6H_4$, 2-alkOCOC_6H_4, or 1-naphthyl amounted to 70–90%; after prolonged heating in pyridine, the yields remained unchanged. Isatogen is apparently not formed in DMF:[8]



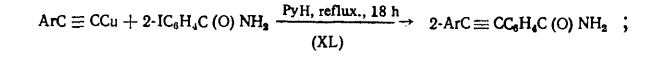
In the reactions of copper phenylacetylide with 1-iodo-8-nitronaphthalene and 2-iodo-2′-nitrobiphenyl only the products of the intramolecular cyclisation of the tolanes (XXXVI) and (XXXVIII) were isolated in a pure form—3-oxo-2-phenylbenzo[*d*,*e*]quinoline *N*-oxide (XXXVII) and 7-oxo-6-phenyldibenzo[*b*,*d*]azepine *N*-oxide (XXXIX):[137]



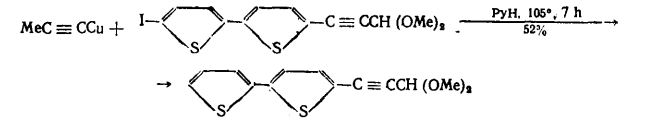
When copper phenylacetylide reacts with *o*-iodocarbamoylbenzene in pyridine, the product is 3-amino-2-phenylindenone; this reaction pathway predominates also in the case of copper *o*-nitrophenylacetylide[84]:



Electron-donating and bulky substituents Ar hinder the cyclisation of the tolanes (XL):[84]

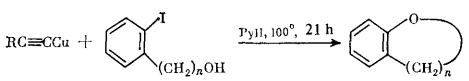


The reaction of COA with aryl halides also suffers from certain limitations. Thus COA having a discrete structure with bulky substituents at the C≡C bond, possessing a strong +*I* effect, do not condense with aryl halides (for example, copper t-butylacetylide does not react with C_6F_5I in pyridine[138]). On the other hand, electron-accepting substituents at the C≡C bond promote the reaction [for example, in the case of ($EtO_2CHC{\equiv}CCu$) [55]]. In the reaction

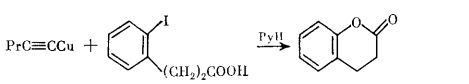


copper methylacetylide apparently behaves as a *C*-metallating agent. It can be assumed that COA exhibit an *O*-metallating activity in the intramolecular cyclisation

reactions[124]



$n = 2$, R = Pr (90%), Ph (100%); $n = 3$, R = Pr (54%), or Ph (85%) ;



We may note that HMP, which is a powerful electron-donating and ionising solvent (Table 1), has not found extensive applications in the synthesis of disubstituted arylacetylenes from COA and aryl halides[140]. It has been shown[141] that the Hal^- and CN^- ions inhibit the main reaction in this instance.

2. 1-Halogeno-olefins and 1-Halogenoacetylenes

The condensation of COA with 1-halogeno-olefins in pyridine or DMF has many features in common with the condensation of the series of compounds RCu, where R = Hal, CN, aryl, alkyl, R'C(O)O (see Refs. 142–144 and the literature quoted therein), Alk_f,[143,145] or SR'.[145] This type of reaction has not been described for silver(I) derivatives.

The interaction of copper(I) derivatives with 1-halogeno-olefins takes place stereospecifically with retention of the initial configuration of both the olefin[142–146] and the COA.[91] As for aryl halides, the reactivity of the halogen then decreased in the sequence I > Br ≫ Cl (F does not react), which is the reverse of that for the direct nucleophilic substitution at an sp^2-hybridised carbon atom[1].

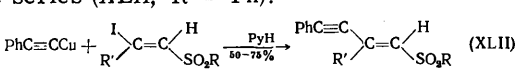
The use of *trans*-chloro(iodo)vinylacetylenes (XLI), which are readily formed when the corresponding vinyl iodides interact with COA in pyridine[145,146], can greatly simplify the synthesis of monosubstituted diacetylenes:



(a) X=Cl, R=Ph, or $PhOCH_2$; (b) X=I, R=Bu, Ph, 4-ClC_6H_4, or 4-IC_6H_4.

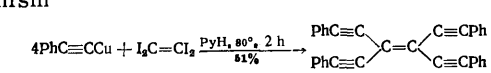
2-*C*-Ethynyl-1-*C*-phenyl-*o*-carbaborane(12) was obtained for the first time from 4-iodo-1-phenyl-*trans*-buten-1-yne.[147]

Electron-accepting substituents at the carbon atoms of the C≡C bond lower the reactivity of 1-iodo-olefins in reactions with COA. Thus the duration of the reaction involving *trans*-1-iodoalk-2-enyl sulphones (XLII) is greater by a factor of 5–10 compared with ICH=CHX (X = Cl or I),[144,148] and sulphones of the propene series (XLII, R' = Me) are more reactive than those of the styrene series (XLII, R' = Ph):[144]

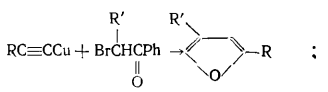


(a) R=4-MeC_6H_4, R'=H, Me, n-Bu, n-C_6H_{13}, or Ph; (b) R=Ph, R'=H, Me, or Ph; (c) R=Me; R'=Me, or Ph; (d) R=Et, R'=Me, or Ph .

Tetra(phenylethynyl)ethylene has been obtained via the mechanism[145]



It has been shown[150] that α-bromoketones react with COA under the same conditions (brief heating to a high temperature without a solvent or in nitrobenzene) as S_N1 halides(benzyl and allyl bromides). Since it has been suggested that the reaction proceeds via a stage involving an α-bromoenol coordinated to copper(I), it is useful to quote examples of such reactions in the present section of the review:



(XLIV)

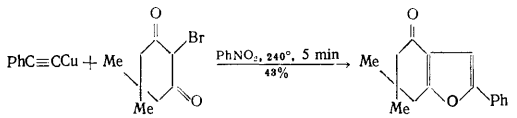
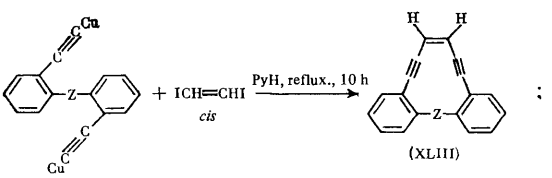


Table 8.

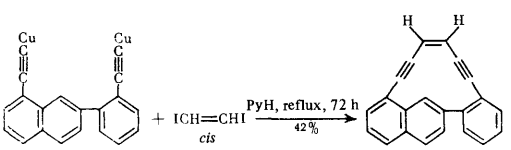
Reaction conditions	R	R'	Yield of (XLIV), %
Without solvent, 140°, 5 min	n-Pr	H	29
Nitrobenzene, 240°, 5 min	Ph	H	54
Nitrobenzene, 240°, 5 min	Ph	C (O) Ph	24

Staab and coworkers used *cis*-di-iodoethylene successfully in the synthesis of benzo[12]annulenes (XLIII)[29,30] and benzonaphtho[12]annulenes[149]:

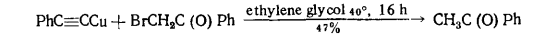


(XLIII)

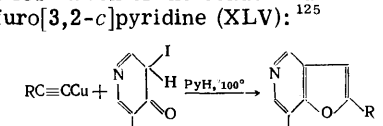
(a) Z = *trans*-HC=CH (17.5%); (b) Z = C≡C (10%); (c) Z = CH_2CH_2 (23%)



In a protic medium copper phenylacetylide promotes the reduction of ω-bromoacetophenone[150]:



The interaction of 3,5-di-iodo-4-pyridone with COA leads to the formation of the condensed heteroaromatic system of furo[3,2-*c*]pyridine (XLV):[125]



(XLV)

R=Ph, α-Py, n-Pr, n-C_6H_{13}, or CH_2CH_2OH

C-Derivatives of copper(I) (the compounds RCu) can be divided into definite groups in relation to 1-halogeno-acetylenes, as in the case of aryl halides. Thus, for

R = Ar, Ar_f,[151-153] and *o*-, *m*-, or *p*-*C*-carboranyl(12),[154] the ethynylation reaction takes place in ether and THF, for R = Alk_f it takes place in DMSO,[155] and for R = CN, it takes place in pyridine[156] and DMF.[157] COA belong to the last group[158].

The interaction of the cuprates $RCu.MgBr_2$ (R = Ar[159] or vinyl[160]) with 1-iodo(bromo)acetylenes is facilitated in the presence of DMF or $(Me_2N)_2C_2H_4$.

Curtis and Taylor[161] used bromopropargyl alcohol to obtain monosubstituted di- and tri-acetylene derivatives:

$$RC{\equiv}CCu + BrC{\equiv}CCH_2OH \xrightarrow{PyH,\ 35-50^\circ} R(C{\equiv}C)_2CH_2OH \rightarrow RC{\equiv}CC{\equiv}CH\ ;$$

R = Me, Ph, Me(OH)CH, $THPOCH_2$, $(EtO)_2CH$, MeC≡C, or 2-(2'-bithienyl).

A new direct ethynylating agent has been described—monobromoacetylene in DMF:[162]

$$Ar(C{\equiv}C)_nCu + BrC{\equiv}CH \xrightarrow{DMF,\ 0^\circ,\ 24\ h} Ar(C{\equiv}C)_nC{\equiv}CH\ :$$

a) n=1, Ar=Ph, 1- or 2-naphthyl

b) n=2, Ar = 1-naphthyl .

3. The Mechanisms of Reactions of COA with Aryl Halides, 1-Halogeno-olefins, and 1-Halogenoacetylenes

In the first studies Castro and coworkers[89,54] already considered the condensation of COA with aryl halides in pyridine within the framework of a general reaction involving nucleophilic substitution in an aromatic ring under the influence of copper(I) compounds, which had been investigated in detail previously[49] in relation to the CuX + ArAl → ArX + CuHal (X = Br, Cl, or CN) exchange. The findings obtained in this study were subsequently confirmed in an investigation of the exchange reactions of CuX with C_6F_5Hal (X = Cl, CN, or OAc),[163] FcHal (X = Cl, Br, or CN),[164,165] and IAr (X = C≡CPh,[124] Ph,[166] 2-furyl, or 2-thienyl[167]) in DMF, pyridine, and quinoline. It was established in all cases that the reactivity of Hal in ArHal decreases in the sequence I > Br ≫ Cl (F does not react), which is the reverse of that for direct nucleophilic substitutions; substituents in Ar have a consistent but weak influence on the rate of reaction, which is of second order overall and of first order with respect to each reactant.

Kinetic and thermodynamic parameters (Table 9) determined for the reaction

$$PhC{\equiv}CCu + IC_6H_4Y \xrightarrow{PyH,\ 100^\circ} PhC{\equiv}CC_6H_4Y + CuI$$

led to certain qualitative conclusions concerning the mechanism[124]: (a) copper phenylacetylide reacts in the dissociated, "monomeric" form (the rate of reaction is described by a second order equation):

$$-\frac{d[IC_6H_4Y]}{dt} = \frac{d[CuI]}{dt} = k_2[PhC{\equiv}CCu][IC_6H_4Y];$$

(b) the ring substitution under the influence of COA is indirectly nucleophilic (although the reactivity of IC_6H_4Y does decrease on passing from Y = NO_2 to Y = OMe or NH_2, the dependence of k_2 on the nature of Y is quantitatively weak); (c) the transition state is distinguished by a high degree of order (high negative activation entropy). According to the authors[124], these data confirm the four-centre concerted mechanism of the reaction of aryl halides with COA, proposed previously[8] (by analogy with the mechanism of Bacon and Hill[49]), which can be represented schematically in the following way in the presence of nucleophilic *o*-substituents in the ring (Y = QR'):[124]

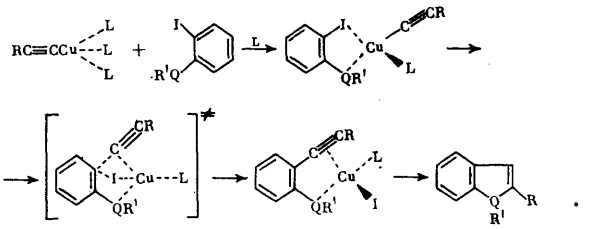


Table 9. Kinetic and thermodynamic parameters (calculated for 25°C) of the reaction

$$PhC{\equiv}CCu + IC_6H_4Y \xrightarrow{PyH,\ 100^\circ} PhC{\equiv}CC_6H_4Y + CuI$$

Y	k_2, litre mole^{-1} s^{-1}			Y	$\Delta F^{\neq}$, kcal	$\Delta H^{\neq}$, kcal	$\Delta S^{\neq}$, e.u.
	o-	*m*-	*p*-				
COOH	$7.0\cdot10^{-2}$	$2.9\cdot10^{-5}$	$4.6\cdot10^{-5}$	H	26	7,2	−63
OH	$8.6\cdot10^{-3}$	$1.3\cdot10^{-5}$	$2.0\cdot10^{-5}$	*o*-NO_2	26	16	−29
NO_2	$2.0\cdot10^{-3}$	$9.1\cdot10^{-5}$	$1.4\cdot10^{-4}$	*m*-NO_2	27	15	−36
OMe	$1.7\cdot10^{-5}$	$1.4\cdot10^{-5}$	$0.85\cdot10^{-5}$	*p*-NO_2	26	13	−41
NH_2	$3.4\cdot10^{-5}$	$1.0\cdot10^{-5}$	$1.4\cdot10^{-5}$				
H	$0.8\cdot10^{-5}$						

A significant factor in this mechanism is the initial I... Cu coordination, the copper atom retaining the tetrahedral configuration.

A similar mechanism has also been postulated by Burdon et al.[105], where the reactive form of COA is regarded as an ion pair, which can be involved in the equilibrium

$$[CuL_AX] \rightleftarrows [CuL_B]^+X^-$$

contact ion pair — separated ion pair

(A = 1 − 3; B = 1 − 4; X=SBu, SPh, C≡CPh) ,

depending on the nature of the solvent ligand L.

The reaction is regarded as a competitive process involving the substitution of ligands at the central copper(I) atom:



It is assumed that only the contact ion pair, in which X is bound strongly to Cu(I) and cannot react independently of the latter, is reactive in the condensation. In the first stage ligands (solvent molecules) are displaced by the substrate ArHal (neutral process); this is followed by the nucleophilic substitution of Hal by X (via a four-centre mechanism), Hal being coordinated to copper(I), which leads to an indirect exchange of Hal for X in the second stage.

The weak dependence of the rate of condensation of COA with Y−ArHal on the nature of Y can be accounted for, within the framework of the four-centre mechanism (by analogy with the mechanism of Sato et al.[168]), by the opposite influence of Y on the rate of attack Hal → Cu and X → C (in Ar), the relative contributions of which determine the overall rate of reaction.

The formation of biaryls, disubstituted butadiynes, and reductive deiodination products from poly(halogenophenyl iodides)[90,106] can be accounted for by the electrophilic

exchange occurring in the intermediate four-centre complex in competition with the nucleophilic exchange and leading to the appearance of the additional condensation agents $ArHalCu$ and $IC{\equiv}CR$.

In order to describe the mechanism of this reaction, one may resort to the radical scheme considered by Atkinson et al.[96] [oxidative addition of a halogen to copper(I) and transfer of the ethynyl ligand from copper(II) to the aryl radical]. In the general case the interaction

$$ArC{\equiv}CCu + Ar_1Hal \rightarrow Ar_1^{\cdot} + Hal{-}Cu{-}C{\equiv}CAr \rightarrow ArC{\equiv}CAr_1 + CuHal$$

should occur in a "cage", although a free-radical reaction pathway can be postulated also for poly(halogenophenyl iodides).

The observation[96] that the reaction is accelerated when the reaction mixture is irradiated by infrared light, unconfirmed by experimental data, has been quoted in support of a radical mechanism. The concept of a radical mechanism has been developed by van Koten and Noltes, who proposed a mechanism with one-electron transfer in an oligomeric copper(I) complex for processes of this kind[169]:

$$(CuX)_n\,(DMF)_m + ArHaI \rightarrow ArHal\,(CuX)_n\,(DMF)_m \rightarrow$$
$$\rightarrow Ar^{\cdot}\,(Cu^{II}XHal)\,(CuX)_{n-1}\,(DMF)_m \rightarrow ArX + CuHal\,(CuX)_{n-1}\,(DMF)_m \quad .$$

In a study of stable arylcopper compounds the same workers isolated and characterised hexanuclear copper clusters having the formula $Ar_4Cu_6X_2$.[25,26,170] The thermolysis of these clusters in DMF leads to biaryls[170] for X = Br or I and to tolanes[26] $ArC{\equiv}CAr_1$ for $X = C{\equiv}CAr$. In principle, such clusters can be formed and can play a definite role in those instances of the condensation of COA with aryl halides where the structure of the initial compounds (for example, for $Ar = C_6X_5$, where X = Cl, Br,[103] or F [99,104,106]) favours the exchange $RC{\equiv}CCu + HalAr = RC{\equiv}CHal + CuAr$. The subsequent course of the reaction (in addition to the condensation steps with liberation of CuHal) is then described by the scheme[26]

$$2RC{\equiv}CCu + 4CuAr \rightarrow Ar_4Cu_6(C{\equiv}CR)_2 \xrightarrow{t^\circ} ArC{\equiv}CR \quad ;$$
$$6ArCu + 2HalAr \rightarrow 2ArAr + Ar_4Cu_6Hal_2 \rightarrow ArAr + 2ArH + 2CuHal + 4Cu^\circ \quad ;$$
$$ArCu \xrightarrow{t^\circ} ArAr + ArH + Cu^\circ \quad .$$

On the other hand, in the general case the "cluster" mechanism is inconsistent with the kinetic data of Castro et al.[124], involves the formation of appreciable amounts of zero-valent copper together with CuHal, and cannot be regarded as a secondary mechanism accompaning the main mechanism of the condensation of COA with aryl halides.

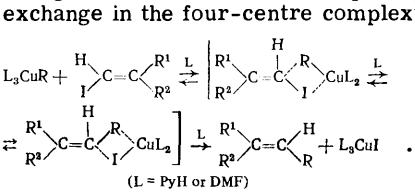
The condensation of COA with ArHal via an intermediate copper(III) compound, in accordance with the mechanism whose prototype is that of the exchange interaction of CuCl with aryl and vinyl iodides (R = Ar or vinyl)

$$CuCl + RI \rightarrow RCu(I)Cl \xrightarrow[-CuI]{+CuCl} RCu + 2CuCl_2 \rightarrow 2CuCl + RCuCl_2 \rightarrow RCl + CuCl \quad ,$$

put forward by Cohen et al.[171], is unlikely if only because the "soft" ligand ArHal cannot stabilise the "hard" Lewis acid copper(III).[172] However, this possibility cannot be ruled out for poly(halogenophenyl iodides).

It has been mentioned, incidentally[173], that copper(II) has a catalytic effect (in the form of a complex of $CuCl_2$ with NH_4Cl) in the reaction of COA with heteroaryl iodides, but the mechanism of the action of copper(II) is obscure.

The condensation of COA with 1-halogeno-olefins is regarded, by an analogy with aryl halides, as a competitive process involving the displacement of the ligand-solvent from the copper(I) coordination sphere by the substrate (1-halogeno-olefin) and the subsequent indirect nucleophilic exchange in the four-centre complex[142,145]:



(L = PyH or DMF)

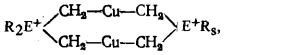
Since such condensation takes place unambiguously with retention of the initial configuration of the olefin and does not lead to dimerisation and reductive deiodination side products, the free-radical reaction mechanism is ruled out, as well as the intermediate formation of the copper(II) compound[142]. The addition of COA to the double bond of the olefin with subsequent elimination of CuHal should also lead to a more complex mixture of reaction products[145].

No information is available in the literature about the mechanism of the condensation of COA with 1-halogeno-acetylenes.

Thus, despite the unambiguous nature of the approach to the mechanism of the direct transfer of the ethynyl residue from copper(I) to the organic substrate (aryl, vinyl), the initial coordination of the halogen atom of the substrate to the copper(I) atom of the "depolymerised" (under the influence of the nitrogen-containing ligand-solvent) form of COA is generally assumed in all the schemes.

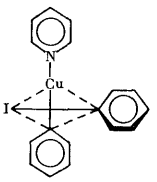
We believe that a common disadvantage of all the schemes discussed above is that they do not reflect the specific features of the COA both as coordination polymers[174] and as copper(I) compounds.

It is known that the polymeric (3c–2e) structure of the σ-aryl derivatives of copper(I) [and apparently silver(I)] is disturbed (as a result of complex formation) by nitrogen-containing electron-donating ligands (pyridine, DMF)[166,167,170]. Subsequent interaction of such complexes, for example, with ArI, can proceed in accordance with a four-centre mechanism via a tetrahedral transition state of type (XLVI).[166] On the other hand, the COA are inert in relation to the action of DMF, pyridine[124], and 2,2- and 4,4-bipyridyls[175] and form discrete (in most instances polynuclear) complexes with strong n-donor ligands—tertiary phosphines[174–176], arsines, stibines[174], cyclic amines[177], *o*-phenanthroline[175], and NH_3,[178] in which the π-interaction of copper(I) atoms with the C≡C bond persists. Evidently the "depolymerisation" of the COA in the L–RHal system (L is an electron-donating nitrogen-containing ligand-solvent, in most cases pyridine or DMF, R = Ar, vinyl, or ethynyl, and the halogen is usually iodine) should occur under the joint influence of both components and should lead immediately to the reaction complex. In view of the wide occurrence and stability of the $Cu^IX_2^-$ bridging anions in the form of discrete species[179] as well as part of the complexes $Y^+CuX_2^-$, where $Y = R_4N$ or Ph_4As for X = Cl, $Y = R_4N$ or Ph_4P for X = Br,[180] and $Y = Cu(PMe_3)_2$ for $X = C{\equiv}CPh$,[181] and the ylids

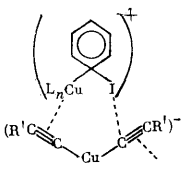


where E = P or As,[182] we suggest that this complex should have the zwitter-ionic structure (XLVII, R = Ar, Hal = I) incorporating the principal features of the structure of the

complex $[PMe_3.CuC{=}CPh]_4$ [181]



(XLVI)



(XLVII)

Since the reactivity of RI in condensation reactions with COA decreases in the series of substituents R ethynyl > vinyl ≫ aryl (alkyl substituents do not react)[1], in which the electronegativity of R and its capacity for the formation of bridge bonds (see below[215]) also diminish, we assume that there is no simple Cu–I coordination in the complex (XLVII). The cationoid component of (XLVII) is a system with a C_{Ar} bridge atom involved in a 3c–2e bond with copper and iodine atoms. The ease of formation of compound (XLVII) and the stability of its cationoid component should evidently increase when n-donor heteroatoms in the aromatic ring are in geometrical proximity to the copper atom (by analogy with stable Cu- and Ag-aryl compounds[170]). Indeed aryl iodides with the NH_2, OH, or COOH substituents in the *ortho*-position as well as 2-iododerivatives of furan, thiophen, and pyridine are much more reactive in reactions with COA than iodobenzene.

The ease of electron transfer from the anionoid component of (XLVII) to the cationoid component is determined by the electron-accepting properties of the ring; this results in the formation (on homolytic dissociation of the ≡C–Cu bond) of the ethynyl radical R′C≡C′. In the cationoid component the 3c–2e bond (Cu–C_{Ar}–I) is converted into a 2c–2e bond (Cu–I) with formation of an aryl radical when the aryl is a weak acceptor, or into a Cu–C_{Ar} bond with formation of the I′ radical species when the aryl is a strong acceptor. Recombination of the radicals in the "cage" should lead to the final products.

Within the framework of the proposed mechanism, the influence of the substituents in Ar on the rate of reaction of ArI with COA is to a large extent cancelled out by their opposed influence on the ease of formation of a complex of type (XLVII) and subsequent one-electron transfer as well as the radical mechanism of the last reaction stage. In this interpretation the condensation of COA with RI (R = Ar, vinyl, or ethynyl) is related to the nucleophilic substitution in diaryliodonium salts catalysed by copper(I) salts, for which the following mechanism has been proposed[183]:

$$Ar_2I^+Cl^- + CuCl \rightleftharpoons Ar_2I^+ + CuCl_2^- \xrightarrow{e} \underset{\text{(ion pair)}}{Ar_2I^+CuCl_2^-} \longrightarrow$$
$$\longrightarrow ArI + ArCl + CuCl \quad .$$

The electron-donating ligand-solvent, which stabilises the cationoid component of the complex (XLVII), should not exhibit a high ionising capacity which would hinder significantly the interaction within the ion pair (XLVII); otherwise (HMP, $\epsilon = 30$, Table 1) the yield of the ethynylation products is sharply reduced[140,141].

Furthermore, the formation of a complex by the ligand-solvent with the copper atom in the cationoid component should influence the oxidation-reduction potential and the strength of the C–Hal bond.

Finally, copper t-butylacetylide[138] as well as silver and gold organoacetylides[174], in which the coordination of the metal atom to the C≡C bond is weak, apparently form under the conditions of reactions of the given type complexes with a nitrogen-containing ligand-solvent, inert with respect to RI (R = Ar, vinyl, or ethynyl), and not structures of type (XLVII); furthermore, one must assume that oxidation of the anionoid component of silver(I) and gold(I) complexes proceeds with greater difficulty than in the case of COA.

4. Compounds with an Element–Halogen Bond

Many inorganic and organoelemental compounds, containing readily polarisable E–Hal bonds, where E is as a rule a nucleophilic heteroatom, react vigorously with COA and SOA in solvents with moderate electron-donating capacities, forming MHal and σ-E-ethynyl derivatives. The simplest examples of reactions of this kind are provided by those of COA with Cl_2, Br_2, I_2, and IBr,[1] for example[147,184]:

$$HCB_{10}H_{10}CC{\equiv}CCu + I_2 \xrightarrow[68\%]{\text{heptane}} HCB_{10}H_{10}CC{\equiv}CI + CuI \quad ;$$
$$Cl_2C{=}CClC{\equiv}CCu + Br_2 \xrightarrow{CCl_4} Cl_2C{=}CClC{\equiv}CBr \quad .$$

Halogens react analogously with SOA:[33,185,186]

$$Me_2CHC{\equiv}CAg + I_2 \rightarrow Me_2CHC{\equiv}CI + AgI \quad :$$
$$C_6Cl_5C{\equiv}CAg + Cl_2 \xrightarrow[90\%]{CCl_4} C_6Cl_5CC{\equiv}CCl \quad :$$
$$4,4'\text{-}(AgC{\equiv}CC_6Cl_4)_2 + Cl_2 \xrightarrow[85\%]{CCl_4} 4,4'\text{-}(ClC{\equiv}CC_6Cl_4)_2 \quad .$$

A method has been developed recently for the synthesis of 1-bromo- and 1-iodoacetylenes via SOA without the preliminary isolation of the latter[187]:

$$RC{\equiv}CSiAlk_3 \xrightarrow[2.\ Hal_2]{1.\ AgNO_3} RC{\equiv}CHal \quad ;$$
(a) Hal=I, R=C(Me)=CHCO(O)Me;
(b) Hal=Br, R=C(Me)=CHCO(O)Me,
CH=CHCO(O)Me, Ph(Et)C(OH), or $Ph_2C(OH)$.

In contrast to the synthesis via COA, the synthesis of 1-chloro- and 1-bromo-acetylenes via SOA is not complicated by the formation of oxidative dimerisation products.

Trisphenylethynyl derivatives of phosphorus, arsenic, and antimony have been obtained by the reaction of silver(I) phenylacetylide with ECl_3 (E = P, As, or Sb) in a benzene–THF mixture[188]:

$$3PhC{\equiv}CAg + ECl_3 \xrightarrow[50\rightarrow70\%]{} E(C{\equiv}CPh)_3 \quad .$$

Copper(I) phenylacetylide reacts only with PCl_3, forming (even in the presence of a large excess of PCl_3) tris-(phenylethynyl)phosphine[1].

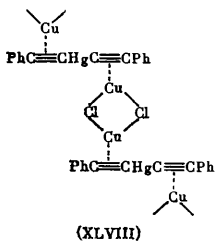
The interaction of silver(I) arylacetylides with $HgHal_2$ leads to bisarylethynyl derivatives of mercury[188]:

$$2RC{\equiv}CAg + HgHal_2 \xrightarrow[\sim 90\%]{THF} Hg(C{\equiv}CR)_2 + 2AgHal \quad :$$
Hal=Cl, Br, or I; R=Ph, C≡CPh .

An analogous reaction has also been described for C_6F_5Ag [52] and for ethoxy-(*p*-tolylimino)methylsilver, i.e. $[p\text{-}MeC_6H_4N{=}C(OEt)Ag]_3$, which is unusually stable in air[189].

In solvents with a moderate electron-donating capacity (THF, alcohol, ether, and acetone) COA react with $HgHal_2$ (Hal = Cl or Br), regardless of the ionising capacity of the solvents, to form complexes having the formal composition $(RC{\equiv}C)_2HgCu_2Cl_2$, to which the structure of

the coordination polymers (XLVIII) was attributed on the basis of Raman spectroscopic data and chemical properties[190]:



(XLVIII)

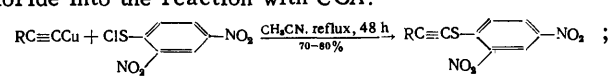
The polymeric complex (XLVIII) has also been obtained by the interaction of copper(I) phenylacetylide with *trans*-β-chlorovinylmercury in CH_3CN and THF and as a result of the oxidative disproportionation of bis(phenylethynyl)-mercury under the influence of copper(II) chloride in the same solvents[190]. On treatment with pyridine, the complex (XLVIII) is converted into bis(phenylethynyl)mercury, while treatment with aqueous ammonia yields copper phenylacetylide (apparently as a result of the selective interaction of the nitrogen-containing ligands with the metal atoms)[191].

Organoelemental halides are beginning to play an increasingly notable role in the chemistry of organic derivatives of copper(I) and silver(I). So far only a few examples of such reactions have been described, for example, the reaction of RM with Me_3SiCl (M = Cu, R = Me_3SiCH_2;[192] M = Ag, R = C_6F_5 [52]), the reaction of ArCu with R_2SnBr_2 [R = Me, Ar = YC_6H_4, where Y = 2-Me_2NCH_2, 2-Me_2N, 4-Me_2N, 2-MeO, 2,6-$(MeO)_2$, or 2,4,6-$(MeO)_3$; R = Ph, Ar = 2-Me_2NCH_2],[193] which take place in weakly polar solvents with a moderate electron-donating capacity. Similar reactions involving COA and SOA take place in more polar media.

In the search for systems with optical manifestations of conjugation via a phosphorus(III) atom, arylbis-(4-nitrophenylethynyl)phosphines were synthesised (with a low yield owing to side reactions)[194]:

$$4\text{-}O_2NC_6H_4C{\equiv}CCu + Cl_2PAr \xrightarrow{THF} (4\text{-}O_2NC_6H_4C{\equiv}C)_2PAr \ ;$$
$$Ar = 4\text{-}YC_6H_4, \text{ where } Y = H, Cl, OMe, \text{ or } NMe_2 \ .$$

Castro et al. introduced 2,4-dinitrophenylsulphenyl chloride into the reaction with COA:[124]



R = n-Pr or Ph.

Organotin compounds are readily ethynylated with the aid of silver alkylacetylides having functional groups[195]:

$$(EtO)_2CHC{\equiv}CAg + BrSnPh_3 \xrightarrow[80\%]{\text{acetone, } 80^\circ} Ph_3SnC{\equiv}CCH(OEt)_2 \ .$$

It has been noted that copper(I) arylacetylides are extremely inert in relation to organotin halides[193]:

$$4\text{-}MeC_6H_4C{\equiv}CCu + Br_2SnMe_2 \xrightarrow[88\%]{17 \text{ days}} 4\text{-}MeC_6H_4C{\equiv}CSn(Br)Me_2 \ .$$

When copper acetylide and 1-*C*-ethynyl-*o*-carbaborane were heated with MeHgBr in a heptane–THF mixture, (*o*-carbaboranyl-1-*C*-ethynyl)methylmercury was obtained[147].

The reactions of covalent transition metal halide complexes with organic derivatives RM, where M = Cu(I) or Ag(I) and R is a powerful inductive acceptor, are of great interest. Thus the halogen atom in the complexes $ClIr(CO)(PPh_3)_2$, $ClRh(CO)(PPh_3)_2$, $ClRh(C_8H_{12})(PPh_3)$, and $Fe(CO)_4I_2$ is substituted by the C_6F_5 group on treatment with C_6F_5Ag in ether[196]; *cis*-$(PPh_3)_2PtCl_2$ reacts with [*p*-$MeC_6H_4N{=}C(OEt)Ag]_3$ in $CHCl_3$, forming a monosubstituted product[189]. In the synthesis of σ-aryl- and σ-carbaboranyl-π-cyclopentadienyldicarbonyliron via the reaction

$$RCu + BrFe(CO)_2(\pi\text{-}C_5H_5) \xrightarrow{\text{ether, THF}} R{-}Fe(CO)_2(\pi\text{-}C_5H_5) \ ;$$
$$R = Ph, 3\text{- and } 4\text{-}FC_6H_4; \ o\text{- and } m\text{-}HCB_{10}H_{10}C{-}; \text{ or}$$
$$o\text{- and } m\text{-}{-}CB_{10}H_{10}C{-} \ ,$$

use was made of aryl and carbaboranyl derivatives of copper(I), apparently in the form of cuprates[197].

Table 10.

$$CuI \xrightarrow{HNEt_2} (HNEt_2)_nCuI \xrightarrow[HNEt_2]{HC{\equiv}CR} (HNEt_2)_nCuC{\equiv}CR + HI{\cdot}HNEt_2 \xrightarrow{MCl} MC{\equiv}CR + (HNEt_2)_nCuCl \ .$$

MCl	R	MCl	R
CpNi(PPh$_3$)Cl *trans*-$(PEt_3)_2PdCl_2$ *trans*-$(PMe_3)_2PtCl_2$	H, Me H, Me, CH_2OH H	*cis*- and *trans*-$(PR'_3)_2PtCl_2$, R' = Et, Bu *cis*- and *trans*-$(PBu_3)_2PtCl_2$	H, Ph C≡CH, 4-HC≡CC_6H_4

The catalytic effect of copper(I) salts in condensation reactions of nickel, palladium, and platinum halide complexes with acetylenes in Et_2NH is attributed to the possibility of the formation under these conditions of amine complexes of COA [198,199] (Table 10). The catalytic reaction proceeds with retention of the initial configuration of the metal atom, which made it possible, in particular, to simplify significantly the synthesis of the *cis*-isomers of platinum(II) complexes which are difficult to obtain:

Under the same conditions, high-molecular-weight polyconjugated polymers, which are stable in air and contain both homogeneous and alternating metal atoms in the chain, were obtained[200,201] via the reaction

$$trans\text{-}(HC{\equiv}CC{\equiv}C)_2M(PBu_3)_2 + trans\text{-}Cl_2M'(PBu_3)_2 \xrightarrow[55\text{–}95\%]{CuI/Et_2NH,\ 20^\circ,\ 20\text{–}50\ h} \rightarrow trans\text{-}[-(PBu_3)_2M(C{\equiv}C)_2(M'(PBu_3)_2(C{\equiv}C)_2-]_n \ ;$$
(a) M=M'=Pt (M_w 20 000); (b) M=M'=Pd; (c) M=Pt, M'=Pd;
(d) M=Pd, M'=Pt (M_w 26 000)

In the reaction involving the bisdiacetyleneplatinum(II) complex products resulting from the monosubstitution of the Cl atoms in *trans*-$(PBu_3)_2M'Cl_2$ (M' = Pt or Pd) were isolated[201].

The mechanism proposed[202] for the catalytic action of the Q = $PdCl_2(PPh_3)_2/CuI/NEt_2X$ system, where X = H or Et, which is highly effective in single-stage syntheses of aryl- and vinyl-acetylenes[202] as well as α-ethynyl ketones[203],

$$RHal + HC{\equiv}CR' \xrightarrow[70\text{–}90\%]{Q} RC{\equiv}CR'$$
$$R = Ar, \text{ Vin or } C(O)R''$$

always includes stages involving the formation of σ-ethynyl derivatives of palladium(II) in accordance with the scheme discussed above:

$$(PPh_3)_2PdCl_2 \xrightarrow{R'C{\equiv}CH,\ CuI,\ NHEt_2} (PPh_3)_2Pd(C{\equiv}CR')_2 \rightarrow$$
$$\rightarrow (R'C{\equiv}C)_2 + (PPh_3)_2Pd(0) \xrightarrow{RHal} (PPh_3)_2Pd\begin{matrix}R\\Hal\end{matrix} \rightarrow$$
$$\xrightarrow{R'C{\equiv}CH,\ CuI,\ HNEt_2} (Ph_3P)_2Pd\begin{matrix}R\\C{\equiv}CR'\end{matrix} \rightarrow RC{\equiv}CR' + (Ph_3P)_2Pd(0) \ .$$

The ethynyl derivatives of benzene, pyridine[202], pyrimidene[204], and pyridazine[205] were obtained by this method; in contrast to COA, the $(PPh_3)_2PdCl_2/CuI$ catalytic system makes it possible to introduce aryl bromides into reactions with terminal acetylenes[202].

The reaction of COA, isolated beforehand, with the complexes $Cl_2Pt(PR'_3)_2$ proceeds similarly to the catalytic process[199,206] (Table 11).

Table 11.

$$RC\equiv CCu + Cl_2Pt(PR'_3)_2 \xrightarrow[60-80\%]{L} (PR'_3)Pt(C\equiv CR)_2$$

R	R'	Isomer	L
Ph	Et	*cis*	Acetone + $Me_2NCH_2CH_2NMe_2$; 20°
Ph	Et	*trans*	ditto
C_6F_5	Ph	*cis*	Boiling benzene
$CH=CH_2$	Et	*cis*	Acetone + $Me_2NCH_2CH_2NMe_2$; 20°
$CH=CH_2$	Et	*trans*	ditto

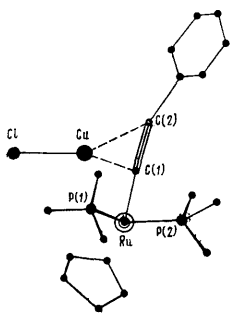


Figure 1. The molecular structure of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2.(C\equiv CPh)CuCl$ (XLIXb); the benzene rings at the phosphorus atoms are not shown.

New types of discrete heteronuclear copper(I) and silver(I) compounds, in which the C≡C groups play an important structure-forming role, have been synthesised by the interaction of COA and SOA with iron, ruthenium, rhenium, iridium, and rhodium halide complexes. These compounds have been partly considered in two reviews[7,207].

The 1 : 1 COA adducts, which have the simplest structures, can be formed as a result of direct exchange and subsequent π-binding of CuHal to the C≡C group[208-211]:

$$RC\equiv CCu + [HalML_n] \rightarrow [L_nM(C\equiv CR)CuHal] .$$

Monomeric ethynyl complexes of ruthenium (XLIX), containing linearly coordinated copper(I) atoms according to X-ray diffraction data (R = Ph) (Fig. 1)[208], have been obtained by the reaction[209]

$$RC\equiv CCu + ClRu(\pi\text{-}C_5H_5)(PPh_3)_2 \xrightarrow{C_6H_6\ \text{reflux.,}\ 20\ h} \underset{(XLIX)}{(\pi\text{-}C_5H_5)Ru(PPh_3)_2(C\equiv CR)CuCl} ;$$

(a) R=Me (55%); (b) R=Ph; (c) R=4-MeC_6H_4 (7%) .

In complexes (XLIX) the π-bond between the copper atom and the C≡C group is resistant to the action of PPh_3 in benzene and is decomposed only by a powerful agent such as the tridentate chelating ligand $MeC(CH_2PPh_2)_3$.[209]

In contrast to (XLIX), in complexes (L)—the dimeric products of the interaction of copper(I) arylacetylides with $(\pi\text{-}C_5H_5)Fe(CO)_2Hal$ (Hal = Cl or Br), a Cu–Cl–Cu bridge bond is formed and the copper atoms have a trigonal coordination environment (Fig. 2)[210-212]:

$$ArC\equiv CCu + HalFe(CO)_2(\pi\text{-}C_5H_5) \xrightarrow{Q,\ \text{relufx.}} [(\pi\text{-}C_5H_5)Fe(CO)_2(C\equiv CAr)CuHal]_2 .$$

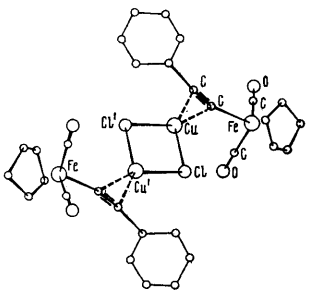


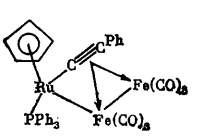
Figure 2. The molecular structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2.(C\equiv CPh)CuCl]_2$ (L, Ar = Ph, Hal = Cl).

Table 12.

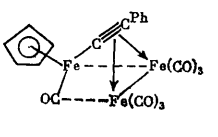
Hal	Q	Ar	Yield of (L), %	Hal	Q	Ar	Yield of (L), %
Cl	Acetone	Ph	42	Cl	THF	C_6F_5	20
Cl	THF	4-MeC_6H_4	27	Br	THF	Ph	10
Cl	THF	4-FC_6H_4	16				

The complexes (L) have been obtained also by specific synthesis from $(\pi\text{-}C_5H_5)Fe(CO)_2(C\equiv CPh)$ and CuHal (the yield is 55% for Hal = Cl and 20% for Hal = Br) in acetone[211]. The use of bromo-derivatives in the direct and specific syntheses lowers the yield of (L) significantly (Table 12).

The thermal decomposition of (L) *in vacuo* results in the formation of ferrocene and diarylbutadiyne[210]. Treatment of (XLIX) and (L) with the carbonyl $Fe_2(CO)_9$ in benzene led to trinuclear clusters with the tentative structures (LI) [210] and (LII):[211]



(LI)

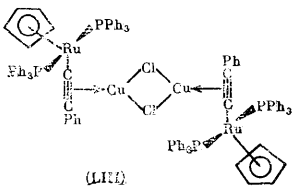


(LII)

In compounds (L) there is no direct interaction between the metal atoms; X-ray diffraction data indicate the presence of a strongly delocalised electron system incorporating the acetylenic fragment, Fe and Cu atoms, and possibly the benzene ring[212].

The structure (LIII), which is analogous to (L), has been attributed to the 1 : 1 dimeric adduct, isolated together with (XLIXb) in the reaction of PhC≡CCu with

$ClRu(PPh_3)_2(\pi\text{-}C_5H_5)$:[209]



(LIII)

The discrete ethynylrhenium complex (LIV) apparently also belongs to the above type of compounds[209]:

$$PhC{\equiv}CCu + cis\text{-}ClRe(CO)_3(PPh_3)_2 \xrightarrow[65\%]{C_6H_6,\ reflux.,\ 6\ h} [(PPh_3)_2Re(CO)_3(C{\equiv}CPh)CuCl]_n \quad (LIV)$$

One may expect that, when $n = 1$, (LIV) will have a structure similar to that of (XLIX) and, when $n = 2$, its structure will resemble that of (L).

Thus it has been established for both (XLIX) [208] and (L) [212] and it has been postulated for (XLVIII), (LIII), and (LIV) that each copper atom is linked centrosymmetrically to one C≡C fragment. It is postulated that the complexes (L) are stabilised as a result of the large contribution of the dative component ($d \rightarrow \pi^*$) to the π-bond between the copper atom and the C≡C group[212].

The 1 : 1 adduct of copper(I) 4-tolylacetylide with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$ (XLIXc) as well as the monoethynyl products of the condensation of copper(I) fluorophenylacetylides with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$ (LV) and $ClRe(CO_3).(PPh_3)_2$ (LVI), which contain no π-linked copper(I) atoms, react with an excess of the corresponding COA, the process being accompanied by a redistribution of the PPh_3 ligand and the formation of diacetylenecopper(I) complexes of a new type[204], for the prototype of the structure of which the zwitter-ionic structure of tertiary phosphine complexes of COA was chosen[181]:

According to X-ray diffraction data[213] (Fig. 3), the complex (LVII) includes a cationoid group, comprising a copper(I) atom asymmetrically π-linked to two C≡C fragments and located in a planar trigonal configuration, and an anionoid group with a central octahedral Re(I) atom; interaction between the metal atoms in (LVII) is unlikely. It is of interest that, among all known phosphine complexes of copper(I), the Cu–P bond length is smallest in (LVII):

$$C_6F_5C{\equiv}CCu + cis\text{-}[ClRe(CO)_3(PPh_3)_2] \xrightarrow{THF,\ reflux.,\ 24\ h} [Cu(PPh_3)]^+[Re(C{\equiv}CC_6F_5)_2(CO)_3(PPh_3)]^- + Re(C{\equiv}CC_6F_5)(CO)_3(PPh_3)_2$$
(LVII), 21% (LVI), 6%

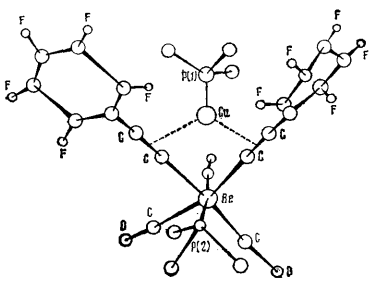
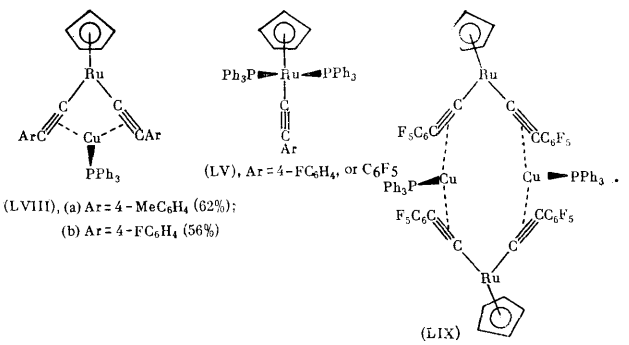


Figure 3. The molecular structure of $[Cu(PPh_3)]^+[Re(C{\equiv}CC_6F_5)_2(CO)_3(PPh_3)]^-$ (LVII); the benzene rings at the phosphorus atoms are not shown.

By analogy with (LVII), a zwitter-ionic structure has been attributed to the main products of reaction of $ArC{\equiv}CCu$ with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$—the monomeric (in benzene) complexes (LVIII) and the dimeric complex (LIX):[209]



(LVIII), (a) Ar = 4-MeC_6H_4 (62%); (b) Ar = 4-FC_6H_4 (56%)

(LV), Ar = 4-FC_6H_4, or C_6F_5

(LIX)

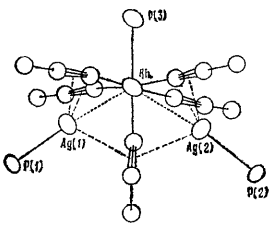
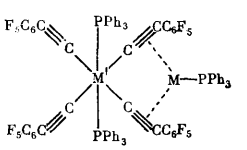


Figure 4. The molecular structure of $PhAg_2(C{\equiv}CC_6F_5)_5.(PPh_3)_3$ (LXI); the pentafluorobenzene rings as well as benzene rings at the phosphorus atoms are not shown.

Together with compound (LVIIIb), the complex (LVa) was isolated from the reaction mixture (yield 5%). The complex (LIX) was obtained after refluxing for 7 h a mixture of $C_6F_5C{\equiv}CCu$ with $ClRu(\pi\text{-}C_5H_5)(PPh_3)_2$ in benzene; an increase of reaction time (to 13 h) results in the formation of (LVb) only. It is suggested that the copper and ruthenium in compounds (LVIII) and (LIX) are univalent and bivalent and that there is no bond between them[209]. The zwitter-ionic complexes $[M'(C{\equiv}CC_6F_5)_4(PPh_3)_2]^-.[M(PPh_3)]^+$ (LX), which are isostructural with (LVIII), have been obtained in a low yield by the reaction of $C_6F_5C{\equiv}CM$ (M = Cu [214] or Ag [215]) with $ClIr(CO)(PPh_3)_2$ in toluene and of $C_6F_5C{\equiv}CAg$ with $ClRh(PPh_3)_3$ in THF and dimethoxyethane (DME).[215]



(LX), (a) M^I = Ir (III), M = Cu (I) or Ag (I); (b) M^I = Rh (III), M = Ag (I)

In the latter case the main product (yield 10%) is an unusual trinuclear complex $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (LXI),[215,216] which has been investigated in detail[215,217].

It contains (Fig. 4) a central Rh atom in a regular octahedral coordination with a PPh_3 molecule and five σ-ethynyl ligands. Each silver atom has a tetrahedral coordination environment, which includes a PPh_3 molecule and three asymmetric π-ethynyl fragments, the *trans*-C≡C group being π-linked to both silver atoms. Data for the coordination environment of the silver and rhodium atoms as well as the absence of interaction between them make it possible to represent structure (LXI) as zwitter-ionic: $[Ag(PPh_3)]_2^{2+}[(PPh_3)Rh^{III}(C{\equiv}CC_6F_5)]^{2-}$. The shortened [compared with other phosphine complexes of copper(I) and silver(I) compounds] P → M bond [M = Cu(I) or Ag(I)] in (LVII) and (LXI) shows that there is a strong M–P d_π–d_π interaction, according to Churchill and DeBoer[217].

The mechanism of the interaction of SOA with $ClRh(PPh_3)_3$ is apparently of fundamentally the same type for all the reactions of COA and SOA with complex transition metal halides examined and is based on a key role of the intermediate $Rh(C{\equiv}CAr)_3(PPh_3)_3$, which is a product of the oxidative addition of two SOA molecules to the complex $Rh(C{\equiv}CAr)(PPh_3)_3$ formed in the first (exchange) stage. Subsequent substitution of the PPh_3 ligands by the ethynyl anion with simultaneous transfer of PPh_3 to the Ag atom should lead to the zwitter-ionic complexes (LXb) and (LXI) according to the mechanism of Abu Salah and Bruce[215].

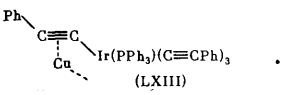
Bruce and coworkers obtained for the first time the ethynyl hexanuclear clusters (LXII) having the general formula $M_4M'_2(C{\equiv}CAr)_8(PPh_2R)_2$ (Table 13) by the reaction of COA [214,218] and SOA [215] with *trans*-$ClIr(CO)(PPh_2R)_2$ and *trans*-$ClRh(PPh_3)_3$ and of COA with *trans*-$ClRh(CO).(PPh_2R)_2$.[214]

Table 13.

M	M′	Ar	R	M	M′	As	R
Cu	Ir	Ph, C_6F_5	Ph, Me	Cu	Rh	Ph, C_6F_5, 4-MeC_6H_4, 4-FC_6H_5	Ph, Me
Cu	Ir	4-MeC_6H_4, 4-FC_6H_4	Ph				
Ag	Ir	Ph, C_6F_5	Ph	Ag	Rh	Ph, C_6F_5	Ph

COA react with *trans*-$ClM'(CO)(PPh_3)_2$ (M′ = Ir or Rh) and *trans*-$ClRh(PPh_3)_3$ on refluxing in benzene or toluene. Reactions of the complexes *trans*-$ClM'(CO)(PPh_2Me)_2$ are better differentiated—in benzene [M′ = Ir(PhC≡CCu) or $Rh(C_6F_5C{\equiv}CCu)$] or DME [M′ = Ir($C_6F_5C{\equiv}CCu$) or Rh(RhC≡CCu)].[214] The reactions of SOA with *trans*-$ClIr(CO)(PPh_3)_2$ take place in toluene and those with *trans*-$ClPh(PPh_3)_3$ proceed in a more polar medium (THF, DME).[215] We may note that the yields of (LXII) decrease on passing from Ir to Rh and from Cu to Ag. The rhodium clusters (LXII) are apparently less stable than the iridium clusters and the extensive formation of diarylbutadiynes in reactions of rhodium halide complexes with COA and SOA is specifically attributed to this fact[214,215]. The enhancement of the electron-accepting properties of the ring in ArC≡CCu and the replacement of PPh_3 by the stronger electron-donating ligand PPh_3Me stabilise the clusters (LXII, M = Cu).[214]

The reaction of the complex PhC≡CCu.PPh_2Me with *trans*-$ClIr(CO)(PPh_3)_2$ proceeds with exchange of the phosphine ligand at the Ir atom and leads to $Ir_2Cu_4(C{\equiv}CPh)_8(PPh_2Me)_2$ with a low yield[214]. According to X-ray diffraction data[218,219], the "skeleton" of the cluster $Ir_2Cu_4(C{\equiv}CPh)_8(PPh_3)_2$ consists of a slightly distorted octahedron in which the equatorial positions are occupied by the Cu atoms and the apical positions are occupied by Ir atoms (Fig. 5). Each $(Ph_3P)Ir$ fragment is σ-linked to four ethynyl ligands and the Ir–C≡CPh system has the transoid configuration (LXIII), unusual for acetylene complexes, which ensures the possibility of the formation of a Cu–Ir bond and the π-interaction of the copper atom with two acetylene groups belonging to different iridium atoms:



(LXIII)

A distinctive feature of the structure of the cluster is a pronounced asymmetry of such interaction.

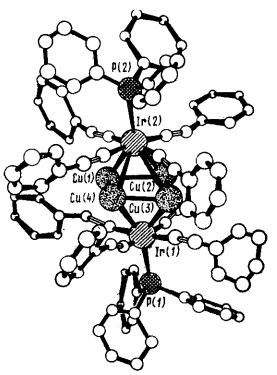


Figure 5. The molecular structure of $Cu_4Ir_2(PPh_3)_2.(C{\equiv}CPh)_8$ (LXII, M = Cu, M′ = Ir, Ar = R = Ph).

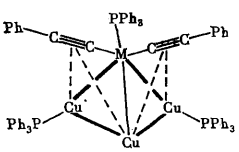


Figure 6. The proposed molecular structure of the cluster $IrCu_3(C{\equiv}CPh)_2(PPh_3)_2$.

It has been suggested[215,244] that all the clusters (LXII) have structures of the same type; the formal valence states of the metal atoms in them are identical: Ir(IV), Rh(IV), Cu(0), and Ag(0). The clusters (LXII) are electron-enriched systems; for M = Cu, it is assumed that the excess electrons are located in the antibonding M′–Cu and Cu–Cu orbitals and are responsible for a bond order of 3/4.[214] A structure (Fig. 6) intermediate between (LXa) and (LXII, M = Cu, M′ = Ir) has been attributed for the electron-deficient cluster $IrCu_3(C{\equiv}CPh)_2(PPh_3)_2$, which has been isolated together with $Ir_2Cu_4(C{\equiv}CPh)_8(PPh_3)_2$ in the reaction of PhC≡CCu with *trans*-$ClIr(CO)(PPh_3)_2$ in benzene[214].

The clusters (LXII, M = Cu, M′ = Ir, Ar = Ph or 4-MeC_6H_4, and R = Ph) react with $Fe_2(CO)_9$ in benzene, forming the octanuclear clusters $Ir_2CuFe_2(C{\equiv}CAr)_8(CO)_8 \cdot (PPh_3)_2$, which retain the Ir_2Cu_4 "skeleton" and do not contain CO bridge groups[214].

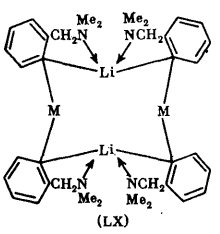
IV. COPPER AND SILVER ORGANOACETYLIDES IN ADDITION REACTIONS

Although the mechanisms of the numerous reactions of COA and SOA with nucleophilic, electrophilic, and 1,3-dipolar compounds considered in this section have not been investigated at all, it is possible to isolate in a purely formal manner the common stage in reactions of this kind where the reactant adds directly to the monomeric R≡C–M (M = Cu or Ag) fragment. In terms of topological features, these reactions can be subdivided into three groups: (1) addition of nucleophiles to copper and silver atoms in COA and SOA; (2) addition of electrophiles and nucleophiles to the ≡C–M (M = Cu or Ag) bond; (3) addition of 1,3-dipolar compounds to the C≡C bond in COA.

1. Addition of Nucleophiles to the Copper and Silver Atoms in COA and SOA

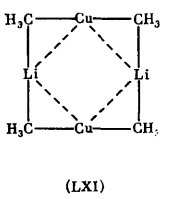
Like organocopper compounds RCu (R = alkyl, vinyl, or aryl), COA react with alkali metal salts in ether and THF to form reactive heterocuprates having the empirical formula $M^+[RC{\equiv}CCuX]^-$ (M = Na, X = CN; M = Li, X = Hal).[3] The reaction of alkali metal organoacetylides RC≡CM with COA (M = Li, Na, or K) and SOA (M = Na or K) in liquid ammonia yielded homoethynyl cuprates and argentates $M[M'(C{\equiv}CR)]_{n+1}$ (M = alkali metal; M′ = Cu(I) or Ag(I); n = 1 or 2), and the available information about them has been surveyed[1]. Mixed ethynyl homocuprates based on COA and various types of organolithium or organomagnesium compounds $M^+[RC{\equiv}CCuR']^-$ (M = Li or MgHal) [3,5] have no analogues in the SOA series.

It has been suggested[170,172] that all organocuprates are structurally similar and have the cluster structure with metal bridge atoms and an electron-deficient 2e–3c M–C–M bond characteristic of Group IB metal compounds. On the basis of experimental data, this type of structure has been proposed for the homocuprates (LX) [170,220] (and the corresponding homoargentates[221]) and the homocuprate (LXI) [172] {cf. with the structure $[CuCH_2SiMe_3]_4$ of a discrete centrosymmetric tetramer consisting of a planar square of Cu atoms, involved in the linear coordination C–Cu–C and the 3c–2e Cu–C–Cu bonds[207]}.



(LX)

M = Cu (I) or Ag (I)



(LXI)

It has been noted that the reactivity of organocuprates is determined by the strength of the M–C–M bridge bond and increases when the latter is weakened in the series N≡C– < C≡CR < aryl < alkyl.[220]

Van Koten and Noltes discovered a fundamentally new structural-chemical type of reactions of COA—the formation of mixed organocopper compounds with ArCu.[24-26] They had shown earlier[222] that, depending on the nature and position of the complex-forming substituent in the ring, arylcopper compounds ArCu react with the halides CuHal to form either 1 : 1 polymers (Ar = 2-$Me_2NCH_2C_6H_4$ or 4-$Me_2NC_6H_4$; Hal = Br) or discrete hexanuclear clusters $Ar_4Cu_6Hal_2$ (Ar = 2-$Me_2NC_6H_4$, Hal = Cl or Br), whose structure has been investigated in detail in relation to $(5\text{-Me-2-}Me_2NC_6H_3)_4Cu_6Br_3$.[170,223] Ethynyl clusters of the type $Ar_4Cu_6(C{\equiv}CR)_2$ (I), where Ar = 2-$Me_2NC_6H_4$, the methods of synthesis of which (including syntheses from COA and ArCu) were examined above, contain an octahedral skeleton of copper atoms, by analogy with the study of Guss et al.[223] (and on the basis of spectroscopic data), the equatorial copper atoms being involved in trigonal coordination with Ar (2e–3c Cu–C bond), the Me_2N group (2e–2c Cu–N bond), and the C≡CR fragment (4e–3c Cu–C bridge bond), while the apical copper atoms are involved in diagonal coordination with Ar (2e–3c Cu–C bridge bond) (Fig. 7)[25].

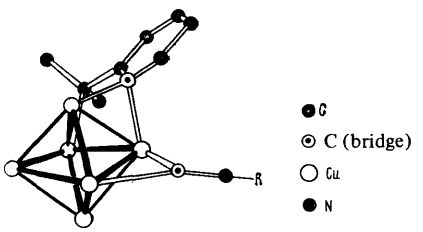


Figure 7. The proposed molecular structure (fragment) of $Ar_4Cu_6(C{\equiv}CR)_2$ clusters (I, Ar = 2-$Me_2NC_6H_4$, R = Ph or 4-MeC_5H_4).

Thermal decomposition of such clusters leads consistently to tolanes[24,26]:

$$Ar_4Cu_6(C{\equiv}CR)_2 \xrightarrow{t^\circ} ArC{\equiv}CR + Ar_3Cu^I_4Cu^0_2(C{\equiv}CR) \rightarrow$$
$$\rightarrow [ArCu^I_2Cu^0_3(C{\equiv}CR)] + 2\,ArCu \rightarrow ArC{\equiv}CR + 4Cu^0 \quad .$$

It has been shown[26] that clusters of type (I) (see Section II) play a key role in 1 : 1 reactions of COA with ArCu of the type

$$RC{\equiv}CCu + ArCu \xrightarrow{DMF,\ 135^\circ} RC{\equiv}CAr + Cu^0 \ ;$$
(a) Ar = 2-$Me_2NC_6H_4$, R = Ph, 2-MeC_6H_4, 2, 4-$Me_2C_6H_3$, 2, 4, 6-$Me_3C_6H_2$, 4-$MeOC_6H_4$, 4-ClC_6H_4, or 4-$O_2NC_6H_4$;
(b) Ar = 4-$Me_2NC_6H_4$, R = 4-YC_6H_4 (where Y = Me, OMe, Cl, or NO_2)

with Ar = 2-$Me_2NC_6H_4$; when Ar = 4-$Me_2NC_6H_4$, the reaction proceeds in all probability via mixed polymeric compounds in which copper atoms form regular bridge bonds with alternating Ar and C≡CR groups. Thus the reaction under consideration reduces to the thermal decomposition of intermediate mixed organocopper compounds, asymmetric dimerisation of the organic residues in the 2e–3c bond with the copper atom occurring more specifically in clusters[26]. It is noteworthy that the symmetrical dimerisation of the arylacetylene residue takes place similarly in the thermal decomposition of copper and silver arylacetylides[224].

The formation of mixed intermediates (of either polymeric or cluster type) can be postulated also in the reaction[225]

$$YC_6H_4C{\equiv}COOH + CH_3Cu \xrightarrow{\text{ether, } 20^\circ,\ 55\text{–}70\%} \left[YC_6H_4C{\equiv}CCOOCu \xrightarrow[-CO_2]{} YC_6H_4C{\equiv}CCu\right] \xrightarrow{2CH_3Cu} \rightarrow YC_6H_4C{\equiv}CCH_3 + Cu^0 \quad ;$$

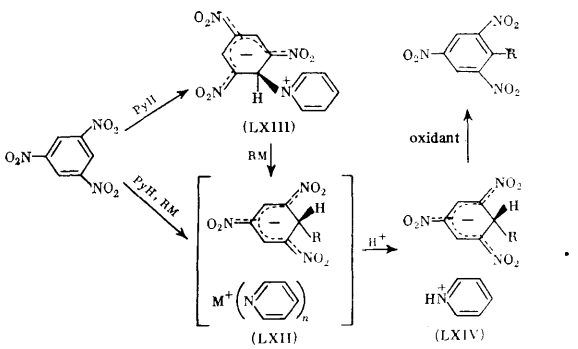
Y=H, 3-Cl, 3-F, 4-Me, or 4-Cl

In this case butylcopper is less reactive than methylcopper; the alkylcopper compounds do not contain lithium salts and were used in proportions of 3 : 1 in relation to arylpropiolic acids. The intermediate formation of COA was demonstrated by a model reaction of the COA obtained beforehand with CH_3Cu:

$$RC{\equiv}CLi \xrightarrow{CuI} RC{\equiv}CCu \xrightarrow[R=Ph\ (75\%),\ \text{or}\ C_{12}H_{25}\ (35\%)]{3CH_3Cu,\ \text{ether, } 20^\circ} RC{\equiv}CCH_3 \quad ;$$

2. The Addition of Electrophiles and Nucleophiles to the ≡C–M (M = Cu or Ag) Bond

Nilsson, Wennerstrom, and coworkers investigated nucleophilic substitution in aromatic compounds by treatment with arylcopper compounds and showed that the compounds RM [M = Cu, R = 2,6-$(MeO)_2C_6H_3$,[226] 2-furyl, 2-thienyl[227], PhC≡C, n-BuC≡C;[228] M = Ag, R = 2,6-$(MeO)_2$.C_6H_3 [229] or PhC≡C [228,229]] react with 1,3,5-trinitrobenzene (TNB) in pyridine to form σ-anionic Meisenheimer complexes (LXII), which coexist with the pyridinium complex (LXIII).



For aryl derivatives of copper and silver, the formation of (LXII) was demonstrated by spectroscopic methods and by the isolation of the pyridinium salts (LXIV) in a pure form (with a yield of 20–40% for M = Cu and 80% for M = Ag). The evidence for the formation of the ethynyl complexes (LXII) is not so rigorous, because it is assumed that their absorption in the visible region is masked by the absorption due to the complexes (LXIII). Treatment of the reaction mixture with dilute H_2SO_4 does not lead in this case to (LXIV) and yield TNB for PhC≡CAg (80% relative to the initial amount), while a more complex set of products is obtained for PhC≡CCu (67% of TNB, 6% of diphenylbutadiyne, 5% of 2,4,6-trinitrotolane, and 6% of its intramolecular cyclisation product 4,6-dinitro-2-phenylisatogen).

The difference between the chemical behaviour of organoderivatives of copper(I) and silver(I) can be clearly traced in relation to the σ-anionic complexes (LXII): thus the complexes (LXII) with M = Ag are more stable and are formed in higher yields than those with M = Cu. The explanation is that the copper(I) complexes (LXII) can be oxidised by atmospheric oxygen or NO_2 groups to R-2,4,6-trinitrobenzenes and RR, while the silver(I) complexes (LXII) require a more powerful oxidant (CrO_3).[226–229]

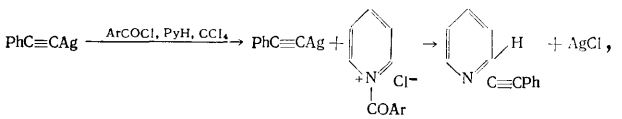
We believe that the acylation of COA and SOA by carboxylic acid halides is the commonest instance of the addition of electrophiles to the ≡C–M bond. This reaction has broad analogies in the chemistry of organocopper(I) and organosilver(I) compounds. Thus (π-C_5H_5)Cu.$P(n\text{-}Bu)_3$, ArCu, C_6F_5Cu,[3] ArOCu,[230] and C_6F_5Ag [52] react smoothly with RCOCl in ether or in the presence of an excess of the acid chloride.

In order to account for the characteristics of the interaction of SOA and COA with acid chlorides (XA), it is convenient to employ the reaction mechanism proposed by Nef for silver phenylacetylide as early as 1899,[231] which is apparently valid for both COA and SOA:

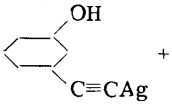
$$RC{\equiv}CM + ClCR' \rightarrow \left[R'{-}\overset{O^+M^+}{\overset{|}{C}}{-}Cl \quad C{\equiv}CR\right] \xrightarrow{-MCl} R'CC{\equiv}CR \quad .$$

Within the framework of this mechanism, the factors promoting an increase of the effective charge on the oxygen atom of XA will favour the reaction. Indeed, the data in Table 14 show that electron-donating substituents R′ and the formation of complexes of XA with $AlCl_3$ and Et_3N constitute in many instances the necessary conditions for the acylation of COA and SOA. It has been noted[232] that 3,5-dinitrobenzoyl chlorides does not react to silver alkylacetylides even in the presence of $AlCl_3$. The acylation of the isomeric *cis*- and *trans*-$C_6H_{13}CH{=}CHC{=}CAg$ proceeds with retention of configuration[233].

In a carbon tetrachloride–pyridine mixture the interaction of silver phenylacetylide with an acylpyridinium salt, and not with XA, becomes the dominant pathway for Ar = Ph and is apparently the only pathway for Ar = 4-$NO_2C_6H_4$ and 3-$NO_2C_6H_4$:[234]



It is of interest to note that this type of reaction does not occur in the systems PhC≡CAg + MeCOCl, n-BuC≡CAg + RCOCl (R = Me or 4-$O_2NC_6H_4$), and



+ RCOCl

(R = Me, Ph, or 4-$O_2NC_6H_4$).

The ethynyl derivative of 1,2-dihydroquinoline was obtained in the reaction of PhC≡CAg with PhCOCl in a carbon tetrachloride–quinoline mixture[234].

The reaction of the copper derivatives of aryl propargyl ethers with PhC(O)Cl under the conditions proposed by the authors of the review[235,236] (benzene, Et_3N, PyH) is accompanied by a prototropic rearrangement with the

resulting α-acetylenic ketones and leads to allenic ketoethers (Ar = Ph or 4-MeC_6H_4):[237]

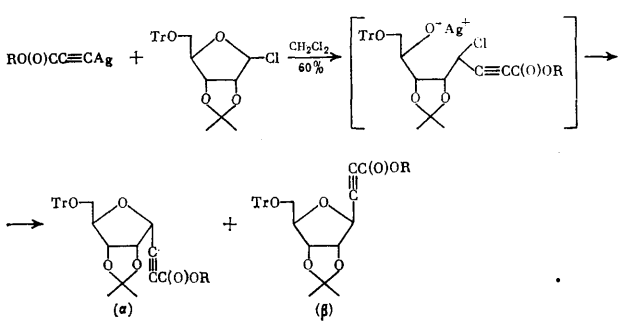
$$ArOCH_2C{\equiv}CCu + PhCOCl \xrightarrow[\sim 30\ \%]{C_6H_6,\ Et_3N,\ PyH} [ArOCH_2C{\equiv}CC(O)Ph] \rightarrow$$
$$\rightarrow ArOCH{=}C{=}CHC(O)Ph$$

Table 14. Acylation of COA and SOA by carboxylic acid halides:

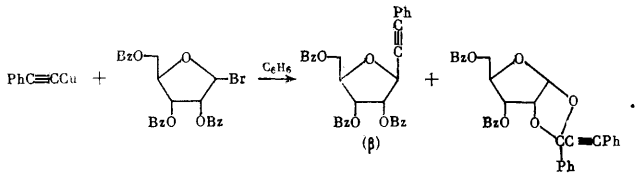
$$RC{\equiv}CM + R'COHal \xrightarrow{L} RC{\equiv}CC(O)R'$$

M	R	R'COHal	L	Yield, %	Refs.
Ag	Bu	MeCOCl	CCl_4	42	232
Ag	Bu	MeCOCl	CCl_4 + $AlCl_3$	44	232
Ag	Bu	$ClCH_2COCl$	CCl_4	57	232
Ag	Bu	PrCOCl	CCl_4	53	232
Ag	Bu	MeCOBr	CCl_4	60	232
Ag	Bu	$BrCH_2COBr$	CCl_4	36	232
Ag	Bu	PhCOCl	CCl_4	0	232
Ag	Bu	PhCOCl	CCl_4, $AlCl_3$	72	232
Ag	Bu	PhCOBr	CCl_4	26	232
Ag	Bu	PhCOBr	CCl_4, $AlCl_3$	67	232
Ag	C_6H_{13}	MeCOCl	CCl_4	61	232
Ag	C_6H_{13}	$ClCH_2COCl$	CCl_4	41	232
Ag	Bu	$EtO(O)C(CH_2)_4COCl$	CCl_4	36	232
Ag	*cis*-$C_6H_{13}CH{=}CH$	$MeO(O)C(CH_2)_6COCl$	CCl_4	—	233
Ag	*trans*-$C_6H_{13}CH{=}CH$	$MeO(O)C(CH_2)_6COCl$	CCl_4	—	233
Ag	Ph	PhCOCl	excess XA	—	231
Ag	Ph	PhCOCl	CCl_4, pyridine	15	234
Cu	Pr	MeCOCl	excess XA	75	124
Cu	Pr	$Ph(CH_2)_2COCl$	excess XA	81	124
Cu	C_8H_{11}	MeCOBr	excess XA	40	141
Cu	C_8H_{11}	PhCOCl	C_6H_5CN	58	141
Cu	Ph	PhCOCl	C_6H_6, NEt_3, PyH	42	235, 236
Cu	Ph	4-BrC_6H_4COCl	C_6H_6, NEt_3, PyH	58	236
Cu	Ph	4-$O_2NC_6H_4COCl$	C_6H_6, NEt_3, PyH	52	236
Cu	Ph	*trans*-PhCH=CHCOCl	C_6H_6, Et_3N, PyH	40	236
Cu	Ph	3-$O_2NC_6H_4COCl$	C_6H_6, Et_3N, PyH	53	236
Cu	Ph	1,4 = $(ClOC)_2C_6H_4$	C_6H_6, Et_3N, PyH	45	236
Cu	Ph	1,3 = $(ClOC)_2C_6H_4$	C_6H_6, Et_3N, PyH	42	236
Cu	1, 3, 5-$Mn_3C_6H_2$	PhCOCl	C_6H_6, Et_3N, PyH	41	236

The reaction of SOA with 2,3-*O*-isopropylidene-5-*O*-trityl-β-D-ribofuranosyl chloride, leading to a 1 : 3 mixture of the α- and β-anomers[238] as in the case of XA, can be represented in terms of the following mechanism (R = Me or Et):



The analogous reaction of copper phenylacetylide with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide is complicated by a secondary process[239]:



Within the framework of the above mechanism of the acylation of COA and SOA by carboxylic acid halides, it is possible to describe the interaction of the complex Et_2PhP. PhC≡CCu with terephthaloyl chloride in THF [236] as well as the interaction of the complexes PhC≡CM (M = Cu or Ag) with CO_2:[12]

$$PhC{\equiv}CM \xrightarrow[2.\ CO_2,\ 80°,\ 50\ atm]{1.\ L,\ THF} [PhC{\equiv}CC(OM) \xrightarrow{3.\ CH_3I} PhC{\equiv}CC(O)OCH_3$$

a) L=PBu_3, M=Cu (50%), or Ag (70%); (b) L = t-BuNC, M = Cu (71%) or Ag (65%).

The reversible insertion of CO_2 in the ≡C–Cu bond has been observed in the system[240]

$$PhC{=}CC(O)OCu \cdot (PBu_3)_3 \underset{}{\overset{DMF}{\rightleftharpoons}} PhC{=}CCu \cdot (PBu_3)_3 + CO_2$$

at atmospheric pressure and a low temperature. The nature of the ligand determines the state of equilibrium: a ligand with a high σ-donor capacity accelerates the decarboxylation [$PBu_3 < PPh_3 < P(OMe)_3$]. Treatment of the reaction mixture with methyl iodide leads to two products: PhC≡CC(O)OMe and PhC≡CMe.

Table 15.

$$ArC{\equiv}CCu + Pt(C_2H_4)(PPh_3)_2 \xrightarrow{L} \left[Ph_3P\!-\!Pt(C{\equiv}CAr)\!-\!PPh_3\ (Cu)\right] \xrightarrow{ArC{\equiv}CCu} \rightarrow Pt(C{\equiv}CAr)_2(PPh_3)_2 + 2Cu^0$$

Ar	L	Yield, %	As	L	Yield, %
Ph	benzene	15	4-FC_6H_4	benzene	12
4-MeC_6H_4	THF	11	C_6F_5	benzene	25

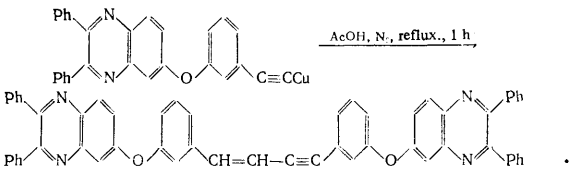
In terms of their formal features, certain reactions of COA, which have no analogy in the chemistry of SOA, can be included in the present section. It is assumed that the reaction of ArC≡CCu with $Pt(C_2H_4)(PPh_3)_2$ proceeds via the intermediate product of the oxidative addition of ArC≡CCu to a zerovalent platinum compound[206] (Table 15). The ethynyl derivative of platinum formed has the *cis*-configuration for Ar = C_6F_5 and the *trans*-configuration in all remaining cases.

The Straus condensation[241,242] or COA can be regarded as addition of the COA complex to a terminal acetylene:

$$2RC{\equiv}CCu \xrightarrow{AcOH,\ N^+} RC{\equiv}CCu \cdot CuOAc + HC{\equiv}CR \xrightarrow{AcOH,\ O_2} \underset{trans}{RC{\equiv}CCH{=}CHR};$$

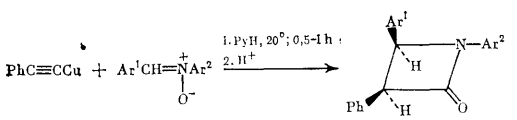
R=Ph, $PhCH{=}CH_2$, or $MeO(O)C(CH_2)_n$, where $n = 0, 1, 8$.

It has been shown recently that this reaction proceeds smoothly also in an oxygen-free medium[243]:



3. Addition of 1,3-Dipolar Compounds to the C≡C′ Bond in COA

It was shown in 1972 that *C,N*-diarylnitrones undergo a cycloaddition reaction with copper phenylacetylide, leading to *cis*-β-lactams, which are difficult to obtain by other methods[244]:



(a) Ar^2 = Ph, Ar^1 = Ph, or 2-YC_6H_4 (where Y = Me or Cl); (b) Ar^1 = Ph, Ar^2 = 4-ClC_6H_4.

A detailed study of this reaction established that it is accompanied by the base-catalysed isomerisation of the initial *cis*-form of the β-lactam into the *trans*-form[245] (Table 16):

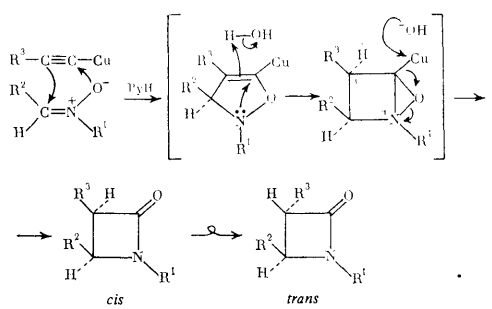
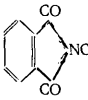
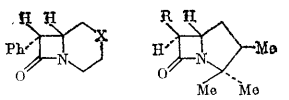


Table 16. β-Lactams derived from COA and nitrones.

R^1	R^2	R^3	Yield of lactam, %	*cis* : *trans*
Ph	Ph	Ph	32	5:3
Ph	Ph	4-MeC_6H_4	50	7:3
Ph	4-MeC_6H_4	Ph	40	4:1
Ph	3-MeC_6H_4	Ph	25	5:4
Ph	2-MeC_6H_4	Ph	25	10:11
Ph	4-$MeOC_6H_4$	Ph	28	*trans*-isomer
4-PhC_6H_4	4-ClC_6H_4	Ph	45	*trans*-isomer
4-MeC_6H_4	Ph	Ph	25	3:4
4-MeC_6H_4	4-ClC_6H_4	Ph	14	5:4
Ph	Ph	Bu	66	12:1
Ph	4-$MeOC_6H_4$	Bu	55	*cis*-isomer
4-MeC_6H_4	4-ClC_6H_4	Bu	9	*trans*-isomer
Ph	4-MeC_6H_4	EtO(O)C	42	*trans*-isomer
Ph	4-MeC_6H_4		31	9:1
Ph	4-ClC_6H_4	ditto	12	*cis*-isomer
Ph	4-ClC_6H_4	$PhN(Me)CH_2$	52	1:1
Ph	4-$MeOC_6H_4$	$PhN(Et)CH_2$	39	*trans*-isomer
Ph	4-ClC_6H_4	4-$EtO(O)CC_6H_4NHCH_2$	75	*cis*-isomer

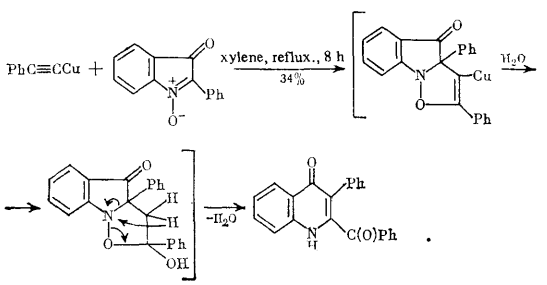
When D_2O was added to the reaction medium, lactams containing the D label in the 3-position were obtained, which demonstrated the incorporation of an H atom from the solvent in this position. The addition of $H_2{}^{18}O$ did not lead to the incorporation of ^{18}O atoms into the final product. Copper n-butylacetylide is less reactive than PhC≡CCu; the *cis*-isomer then predominates in the product. On the other hand, EtO(O)CC≡CCu is more reactive than PhC≡CCu and only the *trans*-isomer is formed in pyridine in this case. The replacement of pyridine by EtOH makes it possible to obtain a 3 : 1 mixture of the *cis*- and *trans*-isomers (R^1 = Ph, R^2 = 4-MeC_6H_4, R^3 = EtO(O)C).

COA based on aminoacetylenes were not isolated beforehand and were used *in situ*. Unstable cyclic nitrones were also introduced into the reaction, which made it possible to synthesise the bicyclic compounds (LXV) and (LXVI):

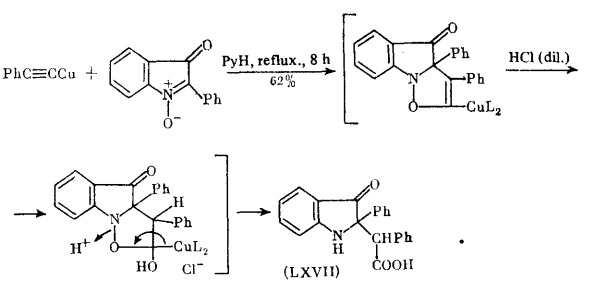


(LXV), X = O or CH_2 (LXVI), R = Ph, Bu, or EtO(O)C.

Aromatic bicyclic nitrones react with COA via two pathways, depending on the solvating (in relation to the C atom) capacity of the medium[74]. In xylene the reaction of copper phenylacetylide with 2-phenylisatogen leads to 2-benzoyl-3-phenyl-4-quinolone:

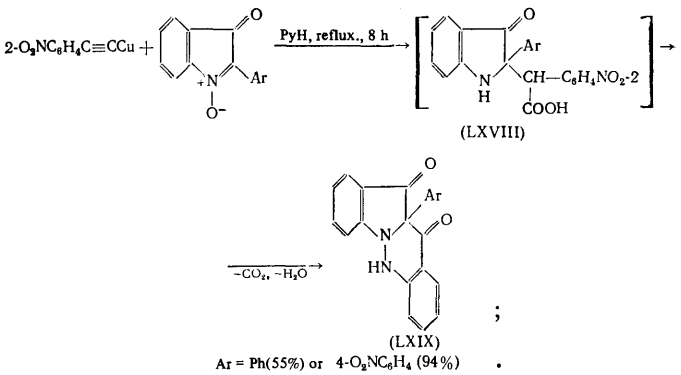


The copper atom is solvated in pyridine, so that the mode of its addition to isatogen is inverted for steric reasons:



The formation of cinnolines (LXIX) from copper 2-nitrophenylacetylide and 2-arylisatogens apparently proceeds via the indolinone (LXVIII), which is analogous

to compound (LXVII):[74]



(LXVIII)

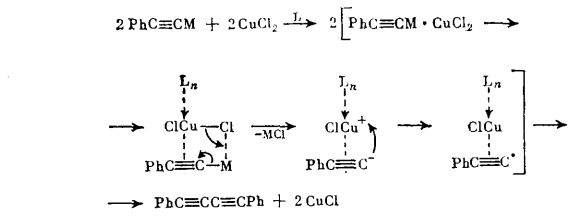
(LXIX)

Ar = Ph(55%) or 4-$O_2NC_6H_4$ (94%) .

V. OXIDATIVE CONDENSATION OF GROUP IB METAL ORGANOACETYLIDES

The oxidative condensation of COA under the influence of O_2 in the presence of coordinating agents of the amine type (strong donors), which stabilise the copper(II) valence state, has been examined in a review[1]. The formation of dicyanogen from CuCN is analogous to this reaction[246].

Extensive experimental data have now accumulated on the use of coordinating agents of moderate electron-donating capacity (Table 1), which destabilise the copper(II) state and stabilise the copper(I) state. Under these conditions, the oxidative condensation of aromatic organolithium and organomagnesium compounds, which lead to either open-chain or cyclic polyarylenes, takes place particularly effectively under the influence of $CuCl_2$.[246,247] The present authors were able to introduce for the first time silver(I) and gold(I) phenylacetylides into the oxidative condensation reaction in THF, acetone, and dioxan[248]:



L = coordinating agent (THF, acetone, and dioxan);
M = Cu(I), Ag(I), or Au(I).

According to this mechanism, the valence state of the metal in the organoacetylide does not change during the reaction and the specific role of copper reduces to a decrease of the oxidation potential of the ethynyl anion and the stabilisation of the ethynyl radical by the π-coordination of Cu...$\overset{C}{\underset{C}{|||}}$, which ensures a convenient geometrical disposition of these radicals for recombination in the "cage". It may be that the dative component Cu $\rightarrow \overset{C}{\underset{C}{|||}}$ predominates in this coordination, which imparts nucleophilic properties to the ethynyl radicals and facilitates their recombination. We may note that, according to Fedenck[249], the free-radical recombination of RC≡C· is thermodynamically unfavourable; it has also been shown that the free radicals PhC≡C· have electrophilic properties and form only tolanes in aromatic hydrocarbons[77]:

$$PhC{\equiv}Cl \xrightarrow{h\nu,\ ArH} PhC{\equiv}CAr \quad .$$

The oxidative dimerisation of COA under the influence of certain transition metal chlorides ($TlCl_3$, $FeCl_3$, $NiCl_2$, $CoCl_2$, $CrCl_3$ [248]) in a fairly wide variety of media (alcohols, nitriles, ether, ethyl acetate, and nitromethane) can also take place in the framework of the above mechanism. The copper(I) chloride formed in the initial stage then remains in the reaction complex as a result of the π-interaction with the C≡C bond.

In solvents with a moderate electron-donating capacity certain oxidants enter into additional interactions with COA. Thus the formation of phenylchloroacetylene in the reactions of copper phenylacetylide with transition metal chlorides[250] can be represented by the following mechanism by analogy[251] with the reaction $R^{\cdot} + CuX_2 \rightleftharpoons [RCuX_2 \rightarrow R^{+}CuX_2^{-}] \rightarrow RX + CuX$:

$$PhC{\equiv}\underset{\underset{Cu^{I}}{|}}{C}{\cdot} + MCl_n \rightarrow PhC{\equiv}CCl + MCl_{n-1} \quad .$$

Thus the composition of the products of the oxidative condensation of COA is determined by the contribution of both reaction pathways of the ethynyl radical. For example, when copper phenylacetylide is treated with bromine (in ether) and chlorine (in CCl_4), a large amount of diphenylbutadiyne is formed together with the corresponding phenylhalogenoacetylenes. On the other hand, the bromination of copper 4-nitrophenylacetylide takes place unambiguously—without the formation of a dimerisation product[1]. In the reaction of tetracyanoethylene (in THF) with 4-$YC_6H_4C{\equiv}CCu$ the main product is phenylethynyltricyanoethylene for Y = H and (4-$YC_6H_4C{\equiv}C)_2$ for Y = I. Tetracyanoquinodimethane oxidises PhC≡CCu smoothly (in CH_3CN) to diphenylbutadiyne[252].

We may point to the syntheses of dicyanodiacetylene by the reaction of NCC≡CCu with $K_3[Fe(CN)_6]$ in a water–benzene mixture[253] and of diphenyltetra-acetylene from PhC≡CC≡CCu under the influence of $CuCl_2$ in water[254] as practical examples of the oxidative condensation of COA in an amine-free medium. The oxidation of the acetylides $Cu(C{\equiv}C)_nR$ (R = H or Cu) (which are in their turn the products of the oxidative dehydropolycondensation of acetylene in an aqueous ammonia solution of $CuCl_2$) by an aqueous solution of $FeCl_3$ or $K_3[Fe(CN)_6]$ yielded a linear polymer (carbine)—a new allotropic form of carbon[255].

It has been shown[249] that the catalytic reaction

$$PhC{\equiv}CH \xrightarrow{PyH,\ CuCl,\ O_2} (PhC{\equiv}C)_2$$

can proceed via the intermediate copper phenylacetylide. Possibly the COA occur in the pathways of catalytic oxidative dimerisation reactions also in many other instances[1].

VI. REACTIONS OF SILVER ORGANOACETYLIDES WITH ARENEDIAZONIUM HALIDES

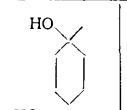
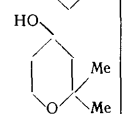
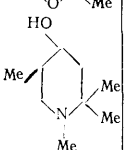
It was shown in 1964 [256] that in an aqueous medium (at pH ~3) arenediazonium chlorides react with SOA of the phenylacetylene series to form azoethynyl compounds (LXX), which are difficult to obtain by other methods:

$$RC{\equiv}CAg + ArN_2^{+}Cl^{-} \rightarrow \underset{(LXX)}{RC{\equiv}CN{=}NAr} \quad .$$

The study of this reaction began with benzenediazonium chlorides containing electron-accepting substituents in the 2- or 4-position in the ring[257,258]. Subsequently the arenediazonium chlorides $YC_6H_4N_2^+Cl^-$, where Y = H,[259] 2-Me, or 4-Me,[260] were introduced into the reaction under the same conditions but using this time SOA of the propargyl type. Thus benzene- and toluene-diazonium chlorides form compounds (LXX) in yields of 8–35% for R = 2-$YC_6H_4C(O)OCH_2$ (Y = H [259] or Cl [260]). Reactions of 4-$YC_6H_4N_2^+Cl^-$ (Y = H or Cl) with silver acetylides derived from 1-ethynyl-1-cyclohexanol, 2,2-dimethyl-4-ethynyltetrahydro-4-pyranol, and 4-ethynyl-1,2,5-trimethyl-4-piperidinol lead to (LXX) in yields of 70–90%.[261] When purified benzenediazonium chlorides and bromides were used and the reaction was carried out in an alcohol–chloroform mixture, the yields of (LXX) with R and Ar belonging to the benzene series were increased greatly and it was possible to isolate the unstable azoethynyl compounds with R = Ph and Ar = Ph and even 4-$MeOC_6H_4$.[262]

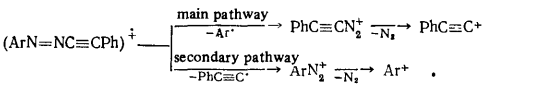
Compounds (LXX) known at the present time and obtained via SOA are listed in Table 17.

Table 17. The azoethynyl compounds $RC{\equiv}CN{=}NC_6H_4Y$ (LXX).

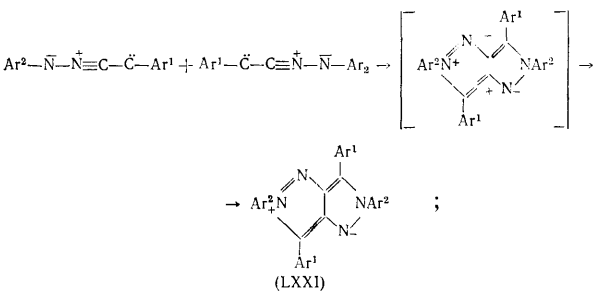
R	Y	Refs.	R	Y	Refs.
Ph	4-Cl, 4-Br, 4-NO_2	257, 258, 262		H, 4-Cl	261
4-$HC{\equiv}CC_6H_4$	4-Br	257			
Ph	2-Cl	258			
4-ClC_6H_4	4-NO_2	258			
4-$O_2NC_6H_4$	4-Cl	258, 262			
Ph	H, 4-I, 4-CN, 4-OMe, 4-EtO(O)C, 2-PhC(O), 2MeO(O)C = 4-Cl	262		H, 4-Cl	261
4-BrC_6H_4	4-Cl, 4-NO_2	264			
4-MeC_6H_4	4-Cl, 4-NO_2	264			
$PhC(O)OCH_2$	H, 2-Me, 4-Me	259		H, 4-Cl	261
2-$ClC_6H_4C(O)OCH_2$	H	260			

The possible mechanisms of the interaction of SOA with arenediazonium chlorides have been discussed[1]; we may note that this reaction has no analogies in the chemistry of organic compounds of copper(I) and silver(I) and is apparently related to the reactions of diazonium salts with powerful nucleophiles—organomagnesium and organozinc compounds[1] and R_fCs [R_f = $C(CR_3)_3$, $(CR_3)_2CF$, or $CF_2CF_2CF_2CF_2$ [263]].

The structure of compounds (LXX) has been investigated by infrared and ultraviolet spectroscopy, NMR, and mass-spectrometry[258,262]. It has been shown that the inclusion of the C=C group in the azobenzene structure leads to a strong bathochromic shift in the ultraviolet spectrum[258]. According to mass-spectrometric data, the fragmentation of (LXX) of the benzene series takes place preferentially with elimination of aryl and not phenylethynyl groups[262]:



The thermal cyclodimerisation of (LXX), leading to derivatives of a new heteroaromatic mezoionic system—2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalenes (LXXI)—leads to great synthetic possibilities for SOA:[262,264]



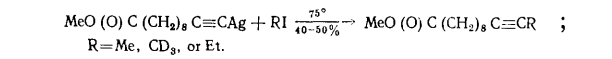
(LXXI)

Ar^1=4-XC_6H_4, Ar^2=4-YC_6H_4; (a) X=H, Y=Cl, Br, or NO_2; (b) X=NO_2, Y=Cl; (c) X=Br, Y=Cl, NO_2; (d) X=Me, Y=Cl, or NO_2 .

Compounds (LXXI) fuse at temperatures in excess of 320°C and are distinguished by high thermal and hydrolytic stabilities: they do not decompose *in vacuo* on heating to 500°C and withstand prolonged boiling in 65% H_2SO_4.[264] A dimer of type (LXXI) is not formed for Ar^1 = Ph and sterically hindered Ar^2 = 2-$PhC(O)C_6H_4$.[262]

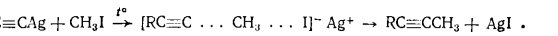
VII. OTHER REACTIONS OF COPPER AND SILVER ORGANOACETYLIDES

In contrast to COA, SOA react with alkyl iodides (on heating in a sealed tube) via the mechanism[265]

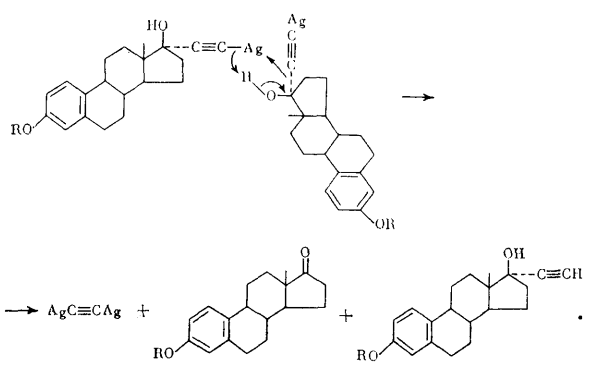


R=Me, CD_3, or Et.

When the reaction is carried out in ether or benzene, a terminal acetylene, corresponding to the initial SOA, is formed together with an alkylacetylene. Since RH and RR are absent from the reaction products, it is assumed that the alkylation of SOA proceeds via a "push-pull" mechanism rather than a free radical mechanism:

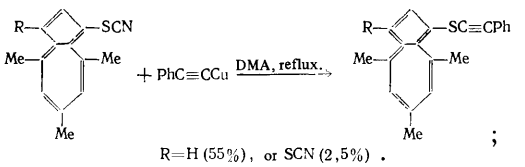


It has been observed that the silver derivative of 17α-ethynyl-17β-hydroxyoestratriene is stable in methanol but disproportionates in aprotic solvents (DMSO, benzene, THF) via the mechanism (R = cyclo-C_5H_9):[36]



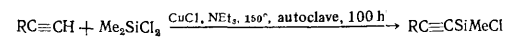
Coppy phenylacetylide reacts with bromocyanogen in an ether–acetonitrile mixture to form PhC≡CCN (yield 60%) and $(PhC{\equiv}C)_2$ (yield 28%); under these conditions, copper methylacetylide is converted into dimethyldiacetylene (yield 65%).[266]

Thiocyanoazulenes react with copper phenylacetylide in dimethylacetamide (DMA) to form thioethynyl derivatives[267]:



R=H (55%), or SCN (2,5%) .

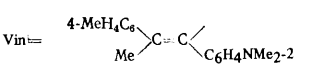
It has been suggested[193] that the catalytic reaction

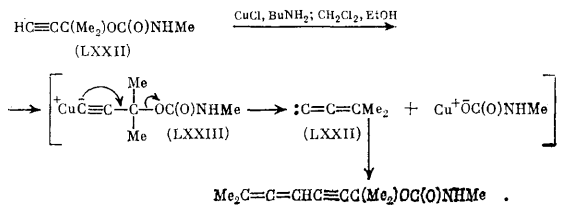


takes place with participation of the intermediate RC≡CCu.

The formation and decomposition of the COA (LXXIII) are adduced to account for the mechanism of another catalytic reaction[268].

By analogy with stable arylcopper compounds[170], the vinyl complex $Vin_2Cu_4Br_2$ has been recently obtained; by treatment with ArC≡CLi, it was converted into a copper(I) vinylethynyl complex $(VinCu_2C{\equiv}CAr)_n$,[269] where





The structure of this complex should differ from that of the arylethynyl clusters $Ar_4Cu_6(C{\equiv}CR)_2$, which has been proposed by ten Hoedt et al.[25] (Fig. 7) and confirmed by X-ray diffraction data[270].

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The data presented in the review show that Group IB metal organoacetylides (in the first place COA) have been firmly incorporated in practical organic syntheses. At the same time the review does not consider numerous instances of the use of COA as homo- and hetero-cuprates, which are widely employed in the synthesis of physiologically active substances (for example, prostaglandins). The reactions of terminal acetylenes and their organoelemental and organometallic derivatives, which take place under the influence of catalytic amounts of copper(I) salts, apparently with participation of COA in a pure form or as cuprates, are of great interest.

It is to be expected that further development of this field of organometallic chemistry will involve a deeper investigation of the mechanisms of the reactions of Group IB metal organoacetylides and the discovery of their new synthetic possibilities.

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Plasteins. Their Preparation, Properties, and Use in Nutrition

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The theoretical and practical aspects of the plastein reaction, which consists in the formation of a gel following the addition of an endopeptidase to a concentrated solution of a partial protein hydrolysate, are examined and the properties and possibilities of using plasteins in nutrition are discussed in detail. It is shown that valuable protein food products can be obtained with the aid of the plastein reaction from proteins with an unbalanced aminoacid composition and from chemically synthesised amino-acids. Other applications of plasteins in nutrition are discussed and the studies carried out hitherto on the mechanism and driving forces of plastein formation are considered.
The bibliography includes 143 references.

CONTENTS

I.	Introduction	897
II.	Conditions and reagents necessary for the plastein reaction	897
III.	Physical properties and structure of plasteins	898
IV.	The influence of various factors on plastein formation	902
V.	Incorporation of various aminoacids in plasteins	906
VI.	The use of plasteins in nutrition	908

I. INTRODUCTION

One of the most important taks of the food industry at the present time is to provide the rapidly growing world population with balanced food products, in the first place protein food products. The proteins used by man as food must be non-toxic, must be free from toxic or other undesirable impurities, and must have a balanced amino-acid composition, i.e. must contain in the first place the essential aminoacids† in the required amounts and proportions[1,2]. Animal proteins fully meet the above requirements, but the sharp increase in their production necessary to satisfy man's needs encounters many economic and technical difficulties. The task of wide-scale employment of proteins derived from non-traditional sources, for example, from sources of plant or microbiological origin, is becoming increasingly urgent.

However, such proteins usually contain toxic and other undesirable impurities and have an unbalanced aminoacid composition. For a wide-scale employment in man's food of proteins from non-traditional sources, it is necessary, in the first place, to free these proteins from impurities and, in the second place, to balance their aminoacid composition. In order to improve the aminoacid composition, it is as a rule necessary to increase their content of essential aminoacids. From the economic point of view, the use of synthetic aminoacids, which can be obtained in large amounts from cheap raw materials, is of greatest promise[3]. Since the presence of free aminoacids in protein food products has a negative influence on their food value, it is necessary for the added essential aminoacids to be present in the final product in the form of polypeptides consisting of one or different aminoacids. One of the ways of obtaining pure protein products with a high food value from contaminated proteins with an unbalanced aminoacid composition and from chemically synthesised aminoacids involves the use of the so-called plastein reaction.

† The aminoacids which are not synthesised in the human organism and must be supplied as food products are referred to as essential. They include isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine. Histidine is an essential amino-acid only for children[2].

Almost 100 years ago Denilevskii found that, when gastric juice is added to a concentrated solution of the enzymatic hydrolysate of any protein, an opaque solution is formed after a time and is gradually converted into a gel[4]. Later Zav'yalov suggested that the reaction be referred to as the plastein reaction and that the gel be called plastein[5]. Up to the end of the 1950's, the plastein reaction was regarded as a possible way of synthesising proteins in the human organism, but, after the discovery of the true mechanism of protein biosynthesis[6-9], studies on plastein formation temporarily ceased. Interest in the plastein reaction grew again at the beginning of the 1970's, because in many instances it proved to be convenient for the preparation of food products.

The plastein reaction is most likely to be used for the following practical purposes: (1) purification of proteins and the formation of protein products with the necessary aminoacid composition; (2) the elimination of the bitter taste from enzymatic protein hydrolysates; (3) the preparation of protein pastes and gels with a high food value for use as fillers in various food products and capable of being used independently as food; (4) the preparation of mixtures of peptides with a definite smell, taste, and other characteristics for use as food additives and odorants.

Various aspects of the plastein reaction have been examined in a number of reviews[10-17]. They show that, although the ways for the practical employment of plasteins have already been defined on the whole, much remains obscure, particularly from the theoretical standpoint. The present review has been written to summarise the studies carried out in this field hitherto and to examine the further prospects of the plastein reaction.

II. CONDITIONS AND REAGENTS NECESSARY FOR THE PLASTEIN REACTION

The plastein reaction takes place in solutions of peptides with a molecular weight between 500 and 1500[5,22-30] at a concentration exceeding 10%[18-21] and a pH of the reaction mixture between 4 and 7.[22,23,31-33]

It can probably be now regarded as established that plasteins are obtained when any endopeptidase acts on hydrolysates of virtually any proteins. The hydrolysates can be obtained both by treatment with any endopeptidase and by partial non-enzymatic hydrolysis of protein. The influence of the properties of the enzyme and protein employed on plastein formation will be examined below in the Section devoted to the influence of various factors on the plastein reaction. One should note that the problem of which properties of a particular plastein can be regarded as common to all plasteins and which depend on the method of synthesis of the plastein has not been studied experimentally hitherto.

III. PHYSICAL PROPERTIES AND STRUCTURE OF PLASTEINS

1. The Structure of Plasteins

The structure of plasteins resembles that of denatured proteins. X-Ray diffraction studies on plasteins revealed the presence of linear polypeptides with close-packed chains extended to the maximum extent[23,34]; structures resembling the secondary and tertiary structures of the protein from the hydrolysates of which they have been obtained have not been detected in the plasteins investigated. The fact that the structure of the initial protein is not restored on plastein formation is confirmed by the absence of enzymatic activity in plasteins obtained from pepsin and trypsin hydrolysates[35] and also by the absence of hormonal activity in plasteins obtained from insulin[36]. The immunological activity of certain plasteins can be explained by the entrainment of a certain amount of the active enzyme and of impurities from the initial protein[11,37-40]. Denaturing agents do not affect the solubility of plasteins, which shows that they do not have an ordered structure[41]. A tertiary structure of the type of an α-helix can probably exist only in plasteins enriched in glutamic acid where the content of the latter is 42% against 24% in the initial protein. The circular dichroism spectra of solutions of such plasteins indicate the possibility of the formation of oligomers with an α-helix structure from glutamic acid residues[42]; the circular dichroism spectra of the usual plasteins do not indicate the presence of such structures. It has been suggested at one time that cyclic polypeptides play a major role in the structure of plasteins[43,44]. Such hypotheses have not been put forward in studies devoted to the plastein reaction in recent years.

Thus the data enumerated above suggest that plasteins consist of a conglomerate of intertwined polypeptide chains with different lengths and structures.

2. The Properties of Plasteins

Despite the fact that plasteins differ from the initial proteins in their secondary and tertiary structures, they resemble proteins in many chemical and physical properties. They are cleaved by various proteolytic enzymes such as endopeptidases and exopeptidases[20,25,42,45-47]. Plasteins have the lowest solubility in the region of the isoelectric point and the dependence of their solubility on the pH of the solution is similar to that for the initial protein[48]. The isoelectric point has been determined for plasteins obtained by treating with α-chymotrypsin the pepsin hydrolysate of soya-bean protein. It has been shown by the method of isoelectric focussing that it is located in the pH range between 3.7 and 4.8.[42,48] Isoelectric focussing of plastein enriched in glutamic acid showed that it has several isoelectric zones in the pH range from 1.5 to 4.0. Plasteins obtained from human serum albumin and casein proved to be electrophoretically homogeneous, in contrats to the initial proteins, and their electrophoretic mobility is somewhat lower than that of the initial proteins. Plasteins synthesised from various proteins differ somewhat in their electrophoretic mobilities[43,49-51]. Like proteins, plasteins react with ninhydrin to form coloured compounds, form complexes with Cu^{2+} ions, and are precipitated by typical protein precipitants such as trichloroacetic acid or various dyes[20,44,52-55].

3. The Molecular Weights of Plasteins

The molecular weights of plasteins have been frequently determined by various methods, but the problem of the molecular weight which plasteins can acquire and the factors on which it depends has not been finally solved. The molecular weights and the methods used for their determination are listed in Table 1.

Table 1. Molecular weights of plasteins and methods of their determination.

Molecular weight	Method	Refs.
Hydrolysate 685-1045, plastein 25000	Polyacrylamide gel electrophoresis (PAGE)	22
Plastein < 21000	PAGE	32
Plastein > 1200	PAGE; precipitation with trichloroacetic acid and dyes	41
Hydrolysate 1280, plastein without additives 12050, plastein enriched in glutamic acid 6240	Amino-nitrogen determined by Van Slyke method	42
Plastein < 1000	Ultracentrifugation	44
Plastein 250000-500000	Ultracentrifugation	57
Plastein ~ 5000	Ultracentrifugation	58
Hydrolysate 1550, plastein 5490	Amino-nitrogen determined by the Van Slyke method	59
Plastein without additives 12000, plastein enriched in glutamic acid 6500	PAGE	60
Plastein enriched in methionine 12000	Amino-nitrogen determined by the Van Slyke method	61
Molecular weight remains unchanged on plastein formation	Chromatography on Sephadex	62
Hydrolysate 1089, plastein without additives 2748, plastein enriched in tryptophan 3019, plastein enriched in threonine 2832, plastein enriched in lysine 2791	Amino-nitrogen determined by Van Slyke method	63
Plastein 5000-6000	Amino-nitrogen determined by the copper complex and cryoscopic methods	64 65
Plastein ~ 1000	Ultracentrifugation	66
Plastein 3000	Cryoscopy	67
It has been shown that plasteins do not contain low-molecular-weight peptides in the absence of substrate	Chromatography on Sephadex	68

One should note that the extremely high molecular weights found by Tauber[57] are probably due to the pronounced ability of plasteins to aggregate; as a result of this, one determines the molecular weight of aggregates linked via hydrophobic interactions and not of the polymeric molecules themselves, from which the plasteins are made up[48]. As regards other molecular weights obtained it is difficult to say what factors are responsible for the observed differences. The only regularity is that plasteins enriched in glumatic acid have the lowest molecular weights. Plasteins are polydisperse[58] and it is most

likely that in the majority of cases their molecular weights are in the range from 5000 to 15 000.[41,42,58-61] However, there exist fairly reliable data showing that the molecular weight does not change on plastein formation[42,52,62]. It appears that, under various process conditions, either the polycondensation reaction, which increases the molecular weight, or transpeptidation, in which the molecular weight remains unchanged, predominates.

It is not possible to state exactly at the present time which particular conditions are responsible for the alteration of the plastein formation mechanism, which leads to the formation of plastein specimens with different molecular weights. The factors suggested in various studies as responsible for the change in the mechanism of the plastein reaction will be examined further in the text below.

4. The Aminoacid Compositions and Solubilities of Various Plastein Fractions‡

Plasteins are on the whole sparingly soluble in all the solvents and mixtures investigated. Unfortunately in the majority of the studies the solubility of plasteins was studied only qualitatively. It can be assumed that at approximately pH 4.0 the solubility of plasteins in water is less than 1%.[42] The higher the concentration of the hydrolysate from which the plastein is formed, the greater the weights of the water-soluble fraction[47].

Table 2. Dependence of the solubility of plastein synthesised with pepsin from the pepsin hydrolysate of soya-bean protein on the pH of the solution[48].

pH	A^*_{600}	pH	A_{600}	pH	A^*_{600}	pH	A_{600}
2.0	0.155	4.5	0.307	6.0	0.253	10.0	0.009
4.0	0.294	5.0	0.267	8.0	0.206	—	—

* Turbidimetric determination; A_{600} is the optical density of the plastein suspension at 600 nm.

The solubility of plasteins has been studied as a function of the pH of the solution, its ionic strength, and the concentrations of urea, guanidinium chloride, and sodium dodecyl sulphate[47,48,53,62]. The dependence of the solubility of plasteins synthesised with pepsin from the pepsin hydrolysate of soya-bean protein on pH is illustrated in Table 2. Evidently the plastein investigated has a solubility minimum at pH ~4, i.e. in the region of the isoelectric point[42]. Presumably all plasteins therefore have a solubility minimum at pH 3–4, because the isoelectric points of the majority of peptides are located in this precise region. Data for the solubilities of plasteins in concentrated acids and alkalies are contradictory. It has been shown[20,53] that certain plasteins dissolve in concentrated nitric and hydrochloric acids. On the other hand, there are data indicating the opposite behaviour[24]. Plasteins apparently dissolve more effectively in concentrated alkalies[20,24,50].

It has been noted that the solubility of plasteins depends little on the ionic strength in neutral solutions, increasing only by 40% with increase of ionic strength from 0.1 to 1.[48] However, it is most likely that the dependences of the solubilities of different plasteins on ionic strength are different. The salting out of plasteins from their solutions in 0.025 M aqueous sodium hydroxide following the addition of NaCl has been noted[53]. In certain cases it has been observed that the dependence of the solubility of plasteins on ionic strength is represented by a curve with a minimum corresponding to an ionic strength of 0.5.[78]

Table 3. Aminoacid composition of various plastein fractions obtained with the aid of pepsin from the pepsin hydrolysate of soya-bean protein[41].

Aminoacid	Aminoacid content in given fraction, wt.%*			
	№ 1	№ 2	№ 3	№ 4
Asp	17.92	11.21	5.42	11.83
Glu	37.22	7.21	5.89	14.90
Lys	5.73	6 03	6.65	3.54
Arg	3.25	3 20	1.12	1.76
His	1.10	1.50	0.62	0.87
Met	0.74	1.70	0.95	0.38
Cys	0.73	2.26	1.21	1.34
Trp	0.63	2 47	0.79	1.72
Gly	5.79	5.26	5.10	3.52
Ser	6.93	5.95	4.75	7.24
Thr	2.05	3.72	2.55	2.53
Ala	2.67	4.95	6.02	3.34
Val	2.00	5.39	8.41	4.60
Leu	4.51	16.91	31.00	22.34
Pro	4.84	10.83	7.70	5.39
Tyr	0.63	1.23	1.32	1.84
Ile	1.76	4.40	7.61	5.96

* Fraction No. 1 dissolves in neutral buffer solutions; fraction No. 2 does not dissolve in neutral buffer solutions but dissolves in sodium dodecyl sulphate solution; fraction No. 3 does not dissolve in either neutral buffer solutions or in sodium dodecyl sulphate solution; fraction No. 4 dissolves in 50% aqueous ethanol but does not dissolve in water.

The solubility of plasteins increases markedly in aqueous solutions of urea, guanidinium chloride, and sodium dodecyl sulphate, the effect of a 6 M aqueous solution of urea or guanidinium chloride being equilvalent to that of a 0.002 M aqueous solution of sodium dodecyl sulphate[37,48]. Certain plasteins[62] readily dissolve also in 50% aqueous acetic acid and in 2 M aqueous sodium perchlorate at pH 6–7. The exact mechanism of the action of these solvents on plasteins and proteins is unknown, but it is extremely likely that they decrease the hydrophobic interactions, which promotes the transfer of non-polar aminoacid residues to the aqueous phase[79,81].

‡ The aminoacid compositions of the initial proteins and various plastein fractions, isolated mainly on the basis of their solubilities in water, have been published[19,41,42,48,52,57,63,69-77]. One should note that the term "aminoacid composition of plasteins" is usually understood as the aminoacid composition of the fraction of the plastein formation product isolated in a particular way. The aminoacid composition of plasteins as a whole should not change. When the aminoacid compositions of various plastein fractions are compared, the influence of the method of fractionation on the aminoacid composition of the fraction is as a rule disregarded, which can lead to incorrect conclusions concerning the nature and mechanism of the formation of plasteins.

The increase of the solubility of plasteins under the influence of substances which reduce hydrophobic interactions suggests that plasteins are sparingly soluble in water precisely owing to the hydrophobic properties of their polypeptide chains. Consequently an increase of the content of hydrophobic aminoacids in the water-insoluble fractions should be observed. The data in Tables 3 and 4 show that there is more of hydrophobic aminoacids in the fraction insoluble in sodium dodecyl sulphate solution than in the fraction insoluble in the buffer solution. The content of hydrophobic aminoacids also increases in the fraction soluble in 50% aqueous ethanol but insoluble in water. In other words, the lower the solubility of the plastein fraction in water, the higher its content of hydrophobic aminoacids regardless of the enzyme and the particular hydrolysate used to obtain the plastein. All these findings suggest that a low solubility of plasteins is due to the accumulation of hydrophobic aminoacids in the sparingly soluble fraction[48].

Table 4. Aminoacid composition of the plastein fraction* soluble in 50% aqueous ethanol but insoluble in water (p), relative to the aminoacid composition of the initial hydrolysate (S)[74].

Amino-acid	S	P	P/S
Asp	1.25	0.85	0.69
Glu	1.35	0.84	0.62
Lys	0.87	0.68	0.78
Arg	0.40	0.39	0.98
Gly	1.00	1.00	1.00
Ser	0.76	0.79	1.04
Thr	0.62	0.57	0.92
Ala	1.31	1.32	1.01
Val	0.76	1.18	1.55
Leu	0.91	2.98	3.27
Pro	0.23	0.68	2.44
Phe	0.45	1.39	3.09
Tyr	0.50	0.60	1.20
Ile	0.62	1.15	1.85

*The plasteins were synthesised with the aid of bioprase from the pepsin hydrolysate of baker's yeast protein. The weight content of glycine was assumed to be unity.

A difference in the aminoacid composition is also observed in the fractions separated from the reaction mixture by ultrafiltration or dialysis, i.e. fractions consisting of peptides having a molecular weight higher than a certain definite value. The data in Table 5 show that in this case the test fraction also exhibits an increase of the content of hydrophobic aminoacids and a decrease of that of hydrophilic aminoacids relative to the initial hydrolysate, although the effect is not so marked.

Thus the solubility of any fraction of plasteins is presumably determined primarily by its aminoacid composition, the plastein formation process involving a rearrangement of the aminoacid residues with formation of a sparingly soluble fraction having an increased content of hydrophobic aminoacids. The possibility of a change in the aminoacid composition of the high-molecular-weight fraction of plasteins on addition of ethyl esters of aminoacids to the initial reaction mixtures has been demonstrated. Typical changes in the aminoacid composition in this instance are presented in Table 6. Evidently the aminoacid composition of the high-molecular-weight fraction can change fairly considerably relative to the aminoacid composition of the same fraction of the given plastein obtained in the usual way - without the addition of the ethyl esters of aminoacids to the reaction mixture. The mechanism of this process and the possible ways of employing such plasteins will be discussed in the following Sections. For the moment, we shall merely point out that the specimens of high-molecular-weight fractions of plasteins obtained, which are enriched in glutamic acid, are much more soluble than either the plasteins with the unchanged composition or the initial protein[42].

Table 5. Aminoacid composition of the high-molecular-weight fraction of plastein obtained by treating the papain hydrolysate of zein with papain, relative to the aminoacid composition of the initial protein[63].

Amino-acid	Aminoacid content, wt.%		γ*	Amino-acid	Aminoacid content, wt.%		γ*
	protein	plastein			protein	plastein	
Asp	4.61	3.91	0.85	Ser	4.42	4.28	0.97
Glu	21.70	13.02	0.60	Thr	2.40	2.13	0.89
Lys	0.20	0.19	0.95	Ala	7.56	8.77	1.16
Arg	1.56	1.74	1.11	Val	3.62	6.20	1.71
His	1.07	1.06	0.99	Leu	20.18	23.49	1.16
Met	1.58	2.04	1.29	Pro	10.93	9.37	0.86
Cys	1.00	0.92	0.92	Phe	6.63	6.98	1.05
Try	0.32	0.33	1.03	Tyr	4.73	5.54	1.17
Gly	1.48	1.52	1.03	Ile	4.39	5.67	1.29

*γ is the ratio of the content of aminoacids in the plastein specimen to their content in the protein.

Table 6. The increase in the content by weight (γ) of certain aminoacids in the high-molecular-weight fractions (molecular weight > 500) of plasteins derived from various proteins* when the ethyl esters of the aminoacids are introduced into the reaction mixture[19].

Amino-acid	Number of protein				
	№ 1	№ 2	№ 3	№ 4	№ 5
Lys	—	1.36	1.69	1.37	9.29
Glu	2.80	—	—	—	—
Met	6.76	8.40	6.0	2.79	—
Try	—	1.81	1.94	1.25	—

*Glutamic acid was used in the form of the α, γ-diethyl ester. When the plastein reaction is carried out in the usual way, the content of these aminoacids in the plastein fraction investigated decreases. Proteins from soya (protein No. 1), clover *Trifolium repens* L. (protein No. 2), seaweed *Spirulina maxima* (protein No. 3), bacterial protein from *Phodopseudomonas capsulatis* (protein No. 4), and gluten (protein No. 5) were used.

The data in Table 7 show that the introduction of glutamic acid makes it possible to increase significantly the solubility of plasteins. The solubility of plasteins enriched in glutamic acid is not influenced by heating the solution at 60°C for 30 min, while the solubility of the usual plasteins changes by a factor of three under the same conditions[42]. This indicates a major contribution of hydrophobic interactions to the formation of plasteins[82-84]. The increased solubility and thermal stability of plasteins enriched in

glutamic acid are probably due to their comparatively low molecular weight and the increased content of glutamic acid as a result of which the hydrophobic interactions in such plasteins are greatly weakened.

Table 7. Dependence on the pH of the solution of the solubilites at room temperature of soya-bean protein (A), plastein synthesised with the aid of papain from the pepsin hydrolysate of soya-bean protein (B), and plastein enriched in glutamic acid and obtained from the same hydrolysate with the aid of papain (C). The glutamic acid contents were 24% in (A) and (B) and 42% in (C)[42].

Specimen	Percentage content of nitrogen in solution relative to the total nitrogen of the sample in a 1% mixture at the pH values indicated							
	1	2	3	4	5	6	7	9
A	75.1	80.2	70.3	12.5	18.3	44.4	83.7	97.5
B	90.2	88.5	81.0	75.0	77.2	80.3	83.5	87.4
C	98.1	98.0	97.6	97.5	97.7	98.0	98.3	98.3

5. The Rheological Properties of Plasteins

The rheological properties of plasteins have been studied systematically in relation to the plastein obtained with the aid of bioprase from the pepsin hydrolysate of soya-bean protein[18]. It was shown that the plastein gels obtained are thixotropic and that the rheological properties change in the direction of greater plasticity and elasticity with increase of the initial concentration of the substrate. This supports the view that plasteins are typical coagulation structures[85], i.e. structures obtained as a result of aggregation via van der Waals forces. The main condition for the formation of coagulation structures is an inhomogeneous mosaic structure–the presence of relatively hydrophobic sections of the chain on the surface of the particles coated by solvation shells. Point contacts–primary units of the structure–arise on these hydrophobic sections. Indeed studies have shown that hydrophobic forces are in fact the cause of gel formation when plasteins are synthesised[41,48].

Thus the gel formation reaction in the preparation of plasteins belongs to the third class of solution–gel transitions[86]. This class of transitions includes processes in which a gel is formed as a result of the loss of solubility by the dissolved substance on altering the temperature or the solvent or when a chemical reaction takes place. In the initial substrate solution all the species are hydrated. A chemical reaction results in the formation of species which exhibit a smaller tendency towards hydration, which makes their aggregation a thermodynamically favourable process as a result of the increase of the entropy of the system[82,83,87].

It follows from the rheological properties of the plastein specimens obtained at different initial substrate concentrations that the most cross-linked structure is observed for specimens obtained from a 35% solution of the hydrolysate[18]. On further increase of substrate concentration, the plastein reaction product solidifies and begins to exhibit the properties of condensation-crystallisation structures[85]. The great strength of the structures obtained from substrate solutions at an initial concentration in excess of 35% is confirmed by the finding that such specimens do not separate into layers with liberation of water even on centrifugation for 30 min at 6500 g at room temperature[18,88]. It is of interest that the plastein gels obtained hardly manifest the phenomenon of syneresis.

The relative viscosities of various plastein specimens have been investigated as a function of their concentration in solution or suspension[18]. The results of the study of the relative viscosities of 5% suspensions of specimens are presented in Table 8. The viscosity of the P-10 specimen is lower than that of the hydrolysate, which suggests that, at a substrate concentration of 10%, the substrate undergoes appreciable hydrolysis and this entails a decrease of viscosity. The sharp fall of the viscosity from the P-35 to the P-45 specimen is apparently a consequence of a qualitative rearrangement of the plastein structure from the coagulation type to the condensation-crystallisation type at an initial substrate concentration in excess of 35%.

Table 8. Relative viscosities η of a 5% solution or suspension of soya-bean protein, the pepsin hydrolysate of soya-bean protein, and various specimens of plasteins obtained from the pepsin hydrolysate of soya-bean protein with the aid of bioprase[18]*.

Specimen	Hydrolysate	Soya-bean protein	P-10	P-20	P-25	P-30	P-35	P-45
η	13	33	9.3	12.5	15	15.8	19	14

*Specimens of plasteins obtained from hydrolysates with initial substrate concentrations of 10, 20, 25, 30, 35, and 45% were investigated. The specimens were designated by P-10, P-20, P-25, P-30, P-35, and P-45 respectively.

In order to understand the driving forces of the plastein reaction, we shall consider how important is the formation of a precipitate and a gel on plastein formation from the thermodynamic standpoint. The thermodynamics of the plastein reaction is influenced solely by the properties of the peptides constituting the substrate, because the enzyme is added in an amount such that it cannot influence significantly the equilibrium position in the system. Comparatively few studies have been made on the thermodynamics of the peptide bond[89-96]. Unfortunately, owing to experimental difficulties, only the thermodynamic parameters of protected dipeptides and certain aminoacid derivatives have been investigated. It can be shown that the hydrolysis of a protected dipeptide is a satisfactory model, from the thermodynamic point of view, of the hydrolysis of a long peptide, which does not alter the ionisation constants of the terminal ionogenic groups. As will be shown in the Section devoted to the influence of the length of the substrate peptide on plastein formation, the synthesis and hydrolysis of peptides of precisely this length occur in the plastein reaction. It has been found that the change in the standard free energy in the hydrolysis of a long polypeptide to shorter peptides is negative and amounts to between -0.5 and 1.5 kcal mole^{-1}. If it is assumed that a mixture of peptides with an average molecular weight of 1000 is used as the substrate and that the concentration of the substrate in the reaction mixture is 50%, then the molar concentration of the substrate is 0.5 M. Taking into account the above standard free energies of hydrolysis, it

is easy to show by calculation that the reaction mixture will contain between 2 and 12% of the dimers of the initial peptides. Clearly the content of peptides with a high degree of polymerisation will be altogether negligible.

Thus the decrease of the free energy of the system on plastein formation cannot be due to the formation of new peptide linkages in concentrated solutions of protein hydrolysates. Consequently the main driving force of plastein formation is the increase of the entropy of the system, which occurs when the hydrophobic aminoacid chains, formed by a rearrangement of the aminoacid residues of the initial peptides, aggregate. Unfortunately a comparison of the aminoacid sequences of the peptides constituting the substrate and the plastein has not so far been made in any instance of plastein formation.

Thus, despite the fact that the rheological properties of plasteins have been investigated for a very limited number of specimens, the studies which have been carried out not only permit the determination of the possible ways of the practical employment of plasteins (see Section VI) but also definite conclusions concerning the driving forces in plastein formation and the structure of plastein molecules.

IV. THE INFLUENCE OF VARIOUS FACTORS ON PLASTEIN FORMATION

For a correct assessment of the influence of various factors on plastein formation, it is necessary to know precisely whether the system is or is not in a state of thermodynamic equilibrium at the instant of measurement. It is still not clear whether the yields of the plastein reactions refer to equilibrium conditions. It has been shown in some studies that the process parameters cease to change with time after 6–8 h,[48] whilst the others it is stated that this requires 2–3 days[73]. No regularities have so far been observed as regards this problem. Nor is it known whether all the system parameters cease to change simultaneously, for example, parameters such as turbidity, molecular weight, amount of the given fraction precipitated from a 10% solution of trichloroacetic acid, etc. However, even if it were known that all the parameters cease to vary at a certain instant, there is still a possibility that the system is then at a local free energy minimum and that the activation barrier to further transformation is very high, i.e. the system is not in a state of equilibrium but is kinetically inhibited. For these reasons, the concept of the yield of the plastein reaction is better replaced by the concept of the efficiency of the plastein reaction, implying by this term the degree of plastein formation under certain specified conditions with respect to the given parameter.

1. Dependence of the Efficiency of Plastein Formation on the Characteristics of the Protein Employed

The efficiency of plastein formation has been investigated[97] as a function of the protein used to prepare the pepsin hydrolysate as the substrate. The efficiency of plastein formation was estimated from the amount of plastein precipitated in a 10% solution of trichloroacetic acid. The experiments were performed at a substrate concentration of 20% and a concentration of α- chymotrypsin, used to synthesise the plastein, of 0.1%. The mixture was incubated for 24 h at 37° C and then a solution of trichloroacetic acid was added at a concentration such that the final concentration was 10%. Under these conditions, the degree of plastein formation from the hydrolysates of different proteins is as follows: 94% for soya-bean protein, 58% for cod protein, 61% for a 9 : 1 mixture of cod and soya-bean proteins, 54% for chlorella protein, 80% for gluten, 35% for casein, 65% for baker's yeast protein, and 93% for petroleum yeast protein.

As stated above, the formation of the water-insoluble fraction is one of the main driving forces in the plastein reaction. Hydrophilic substrates do not form plasteins in high yields, because the products of the plastein reaction are then soluble and are difficult to remove from the system[97,98]. Thus attempts to synthesise plasteins from a highly hydrophilic protein (gelatin) were unsuccessful[53,98]. On the other hand, if the hydrolysate is too hydrophobic, the product is readily precipitated before the plastein formation reaction reaches an advanced stage[63].

Table 9. Dependence of the efficiency of plastein formation on the molecular weight of the substrate[22].

Molecular weight	Percentage content of fraction precipitated with 10% trichloroacetic acid after incubation		Molecular weight	Percentage content of fraction precipitated with 10% trichloroacetic acid after incubation	
	with enzyme	without enzyme		with enzyme	without enzyme
>1043	6.6	3.3	685	33.2	0.0
1043	23.0	0.0	<685	0.0	0.0

It has been shown[99] that, knowing the yield of the plastein reaction with respect to the high-molecular-weight fraction of the hydrolysates of individual proteins, it is possible to predict the component ratio for which the yield of the plastein reaction with respect to the high-molecular-weight fraction will be a maximum. For this purpose the parameter β/α was introduced, β being the degree of insolubility of the plastein, defined as the ratio of the nitrogen insoluble in 20% aqueous acetone solution to the overall nitrogen content in the plastein and α the yield of the plastein reaction, defined as the ratio of the amount of nitrogen precipitated in 10% trichloroacetic acid solution to the overall nitrogen content in the plastein.

It has been shown in relation to extensive experimental data that, whatever the substrates or their mixture, the plot of the yield of the plastein reaction with respect to its high-molecular-weight fraction against the parameter β/α is bell shaped with a mixmum at $\beta/\alpha \simeq 0.5$. The dependence of the parameter β/α on the ratio of the contents (by weight) of the two substrates is then linear. Thus the ratio of the substrates in the mixture for which the plastein reaction has a maximum yield with respect to the high-molecular-weight fraction can be calculated from the formula

$$x/y = \frac{0.5 - \beta/\alpha\,(x)}{\Delta\beta/\alpha},$$

where x/y is the ratio of the weight fractions of the two substrates, $\beta/\alpha(x)$ the value of the parameter β/α for the substrate x, and $\Delta\beta/\alpha$ the difference between the values of the parameter β/α for the substrates x and y.

Thus, when the parameter β/α is used, it is possible to select a mixture of substrates giving the maximum yield of the plastein reaction with respect to the high-molecular-weight fraction.

2. The Influence of the Structure of the Substrate on the Efficiency of Plastein Formation

We shall now consider the requirements which must be met by the peptides in the substrate in order that plastein formation should be successful to the maximum extent.

The efficiencies of the fractions of soya-bean hydrolysate of different molecular weight in the plastein reaction have been compared[22]. The initial concentration of the substrate was 35% and the ratio of the weight concentrations of subtilisin BPN' and the substrate was 0.01. The reaction mixture was incubated for 24 h at 37° C. The intensity of plastein formation was estimated from the amount of precipitated fraction in 10% trichloroacetic acid solution. The results of the study are presented in Table 9, which leads the conclusion that plastein formation takes place most effectively in the system containing peptides consisting of 5–8 aminoacid residues[5,22–24]. In addition, it was found that the plastein reaction proceeds most effectively when the degree of hydrolysis of the initial protein is such that 20% of the hydrolysate (by weight) is precipitated in 10% trichloroacetic acid solution[10,15,25]. The synthesis of plasteins and peptides from pure aminoacids was unsuccessful[26,27]. The fact that free aminoacids do not participate in the plastein reaction has been confirmed by numerous experiments, which have demonstrated the impossibility of enriching the plastein in aminoacids when the latter are introduced into the reaction mixture in a free state[52,94] and also by the fact that the plastein is formed more successfully from the non-dialysable fraction of the protein hydrolysate[52].

There exists a view that, with increase of the molecular weight of the substrate, the mechanism of plastein formation changes from polycondensation to transpeptidation[23]. One of the incomprehensible features of the plastein reaction is the nature of the change of the content of amino-nitrogen in the reaction mixture when plasteins are formed. It was noted that, in the process investigated, the amount of primary amino-groups can decrease[47,64], increase[25,62], remain unchanged[52,101], and pass through a minimum[23,32,68]. It is very likely that, when 5–8-membered peptides are used, a polycondensation reaction, accompanied by a decrease of the content of primary amino-groups in the reaction mixture, takes place.

Subsequently, after the attainment of a critical length of the peptides, mainly a rearrangement of the aminoacid residues occurs with formation of sparingly soluble peptides and the liberation of freeamino acids and low-molecular-weight peptides[23,73]. As a result of this, the content of primary amino-groups in the reaction mixture increases. It may be that the contradictory data concerning the changes in the content of amino-nitrogen on plastein formation can be accounted for by using substrates of different molecular weight.

The problem of which aminoacids should make up the peptides in order that plasteins can be formed from the latter is very interesting. In the previous section it was stated that proteins should be moderately hydrophobic in order to produce hydrolysates capable of giving rise to plasteins in a high yield. Plastein-active peptides were first identified by Determann and coworkers[102–104], who showed that the peptides forming the plastein under the influence of pepsin and α-chymotrypsin have the following structure:

H—Met—Thr—Leu—Leu—(Leu, Thr, Val)—Thr—Ser—Met—Leu—OH
H—Tyr—Ile—(Glu, Gly, Phe)—(Glu, Ile)—Phe—OH
H—Tyr—(Asp, Val)—Glu—Glu—Ile—OH
H—Ile—Asp—Val—Glu—Glu—Ile—OH

The structure of these peptides shows that the efficiency of plastein formation is determined primarily by the terminal aminoacid. This hypothesis was first put forward by Virtanen et al.[51].

In order to establish a relation between the structure of peptides and their ability to form plasteins, studies were performed using as substrates various peptides having a definite structure[24,28–30,105,106]. The plastein reaction was carried out with the aid of pepsin at pH 4.0 and chymotrypsin at pH 8.6. A 25–50% solution of the substrate, incubated with the enzyme at 37° for 24 h, was used. The high-molecular-weight fractions of the plasteins were separated by centrifugation or were precipitated with trichloroacetic acid. The plasteins obtained under the influence of pepsin have a molecular weight of ~2250 with an average degree of polymerisation of 2.5, which was established by the photometric determination of the amount of terminal aminoacid residues in the form of dinitrophenyl derivatives[30]. The authors explain the low degree of polymerisation by the poor solubility of the resulting plasteins. It was found that, under the above conditions, plasteins are formed by peptides having the following structure[29]:

H—L—Tyr—L—Leu—Gly—L—Glu—L—Phe—OH
H—L—Tyr—L—Leu—Gly—D—Glu—L—Phe—OH
H—L—Tyr—L—Leu—Gly—L—Val—L—Phe—OH
H—L—Tyr—L—Leu—Gly—L—Lys—L—Phe—OH
H—L—Tyr—L—Ile—Gly—L—Lys—L—Phe—OH
H—L—Tyr—L—Lys—Gly—L—Glu—L—Phe—OH
H—L—Tyr—L—Lys—Gly—L—Lys—L—Phe—OH
H—L—Tyr—L—Leu—Gly—L—Glu—L—Tyr—OH
H—L—Tyr—L—Leu—Gly—L—Glu(NH_2)—L—Tyr—OH

On this basis, it was concluded that aminoacid residues located in the centre of the peptide chain have no influence on the plastein reaction catalysed by pepsin and chymotrypsin. It is also unimportaint whether the peptide is basic, neutral, or acid.

The influence of chain length and of the nature of *N*- and *C*-terminal aminoacid residues on the plastein reaction has been investigated[24]. For this purpose, the following peptides were synthesised:

H—Ala—Leu—Gly—Glu—Phe—OH
H—Tyr—Leu—Gly—Glu—Ala—OH
H—Ala—Leu—Gly—Glu—Ala—OH
H—Tyr—Leu—Ala—Glu—Glu—Phe—OH
H—Tyr—Leu—Glu—Phe—OH
H—Tyr—Glu—Phe—OH

It was found that, for a peptide to be capable of involvement in the plastein reaction catalysed by pepsin or chymotrypsin, it is necessary that it should have hydrophobic *C*-terminal aminoacids and should consist of at least four aminoacid residues.

Thus two main requirements must be met by the substrate of the plastein reaction when the plastein is synthesised with the aid of pepsin or chymotripsin: it must consist of peptides formed from 5–8 aminoacid residues and in addition the aminoacid residues at the ends of these peptides should be hydrophobic. The possible reason why the plastein reaction takes place most successfully with peptides of a definite length is as follows. According to the thermodynamics of the peptide linkage, the polycondensation of peptides is thermodynamically more favourable than the polycondensation of aminoacids[89–96]. However, in solutions of peptides at identical weight concentrations the concentration of amino- and carboxy-groups is lower the higher the molecular weight of the substrate. In solutions

of peptides consisting of 5–8 aminoacid residues there is probably, on the one hand, still a fairly high concentration of amino- and carboxy-groups and, on the other, the formation of a peptide linkage between such peptides is already more favourable than between aminoacids. The fact that plastein formation requires the presence of hydrophobic aminoacids at the ends of polypeptides can be accounted for by two causes. Firstly, the thermodynamics of the peptide linkage can be such that the bond formed by hydrophobic aminoacids is thermodynamically most favourable. One can hardly expect a large difference between the thermodynamic parameters of the bonds formed by different aminoacids[89-96]; at the same time, it is known that the majority of proteolytic enzymes exhibit a greater or smaller specificity with respect to hydrophobic aminoacids[107,112]. It is therefore most likely that the limitations imposed on the structure of plastein-active peptides are due to the specificity of the enzymes employed. This hypothesis is supported by the fact that trypsin, the enzyme which hydrolyses and synthesises solely bonds formed by the carboxy-groups of lysine and arginine[113], does not exhibit a plastein-forming activity[114]. Nor is it possible to obtain plasteins from hydrolysates produced under the influence of trypsin[115].

3. The Influence of Substrate Concentration on Plastein Formation

The dependence of the efficiency of plastein formation on substrate concentration has been studied[18] using different enzymes. Plasteins were synthesised from the pepsin hydrolysate of soya-bean protein at substrate concentrations of 5, 10, 20, 30, 40, and 50% and for enzyme and substrate concentration ratios (by weight) in the range 0.01–0.03. The reaction mixture was incubated for 24 h at 37°C. The following enzymes were used: chymotrypsin, pepsin, coronase, bioprase, and molsin. The pH of the reaction mixture was maintained at values indicated by Yamashita et al.[114]. The efficiency of plastein formation was estimated from the weight of the fraction precipitated with a 10% solution of trichloroacetic acid. It was shown that in all cases the yield of plastein has a maximum at a substrate concentration between 30 and 40%. At substrate concentrations less than 6–8%, the substrate hydrolyses[18,19].

Analogous results were obtained in studies[23,44] involving the formation of plastein under the influence of pepsin from a pepsin hydrolysate of zein and in studies[20,21] on the preparation of plastein under the influence of pepsin and papain from the pepsin and papain hydrolysates of egg protein. According to modern views on the mechanism of plastein formation, the conclusion that the optimum substrate concentration for plastein formation is 30–40% and that plastein formation does not occur at a substrate concentration below 6–8% is probably common to plasteins obtained from any proteins under the influence of any enzymes.

4. The Influence of the Enzyme and Its Concentration on the Efficiency of Plastein Formation

As already mentioned, a very large number of proteolytic enzymes of different origin have been used in the plastein reaction. The only feature which these enzymes have in common is that they are all endopeptidases. The efficiencies of plastein formation under the influence of various enzymes have been compared systematically[97]. The data compiled in Table 10 show that α-chymotrypsin is most effective in the plastein reaction, while other enzymes are less effective. One should note that the efficiencies of plastein formation listed in Table 10 for a series of enzymes (for example papain and pepsin) conflict with the wide use of these enzymes for the preparation of plasteins.

Table 10. Comparative efficiencies* of various enzymes in the plastein reaction[97].

Enzyme	Yield of plastein, %	Enzyme	Yield of plastein, %
Endopeptidases:		Microbiol proteases:	
α-chymotrypsin	95.0	bioprase	85.5
bromelain	29.0	coronase	52.1
papain	26.8	molsin	21.3
pepsin	20.0	pronase	36.3
trypsin	21.9	prozime	77.0
Exopeptidases:		rapidase	20.0
aspergillocarboxypeptidase	20.0	thermoase PC-10	32.3
carboxypeptidase A	26.5		20.0
leucine aminopeptidase	22.1		

*The plasteins were synthesised from the pepsin hydrolysate of soya-bean protein. The efficiency of plastein formation was estimated from the weight of the plastein fraction precipitated in 10% trichloroacetic acid solution.

The absence of plastein-forming activity in exopeptidases can be explained by the fact that the linkage between peptides is thermodynamically more favourable than the linkage between a peptide and an aminoacid. The different plastein-forming activities of different endopeptidases can be explained only by the fact that at the instant of the measurement the yield of the plastein reaction is still far from equilibrium, because the enzyme, acting as a catalyst, cannot influence the equilibrium position in the system. The reason for the absence of plastein-forming activity of trypsin was examined above.

The influence of enzyme concentration on the efficiency of plastein formation has been studied[20,31,33,47,53]. It was shown that, firstly, in the plastein reaction the enzyme concentration can be approximately the same as the hydrolysis of proteins – up to 1 wt.%, and secondly, that the efficiency of plastein formation depends only very slightly on the enzyme concentration. Thus with increase of the concentration of the enzyme (pepsin) from 0.1 to 8%, the amount of the plastein fraction derived from the pepsin hydrolysate of egg albumin and insoluble in the reaction mixture increases from 13.1 to only 33.3%.[53] In a study of the synthesis of plastein by this procedure[31] a relation was found between the weight of the insoluble fraction and the weight of the enzyme employed: $P = 13.9E^{0.213}$, where P is the weight of the plastein fraction obtained and E the weight of the enzyme employed. An analogous result was obtained in a study[47] where plastein formation from the pepsin hydrolysate of zein under the influence of pepsin was investigated. The efficiency of plastein formation was estimated in this instance from the decrease of the content of amino-nitrogen, determined by the copper complex method[116].

The influence of enzyme concentration on the rate of plastein formation was hardly considered. It has only been stated in one study[20] that the rate of the plastein reaction, determined as the increase with time of the amount of nitrogen precipitated from a 2.5% solution of trichloroacetic acid, is proportional to the square root of enzyme concentration.

Substances which inhibit the activity of the enzyme employed retard or altogether terminate plastein formation[20,25,78,117].

When the influence of enzymes on the plastein reaction is considered, the following factors must be taken into account. It is known that all enzyme preparations contain a certain amount of inactive protein; the concentration of enzymes in solution, found from their weight concentrations, does not therefore represent their true concentration (normality) in solution. In order to determine the normality of enzyme solutions, it is necessary to find the concentrations of their active centres. However, no studies have been made on plastein formation with enzymes of known normality.

5. Dependence of the Efficiency of Plastein Formation on the pH of the Reaction Mixture

The dependence of the efficiency of plastein formation on the pH of the reaction mixture has been studied[22,23,31-33] The dependence of the plastein reaction on the pH of the solution was first investigated for the plastein synthesised using pepsin from the pepsin hydrolysate of egg albumin[31]. The efficiency of plastein formation was determined from the weight of the filtered fraction. It was shown that in this case the insoluble plastein fraction is formed most effectively at pH 4.0. The same pH optimum was found for the plastein reaction catalysed by pepsin[23].

The pH dependence of the rate of plastein formation from a pepsin hydrolysate of soya-bean protein has been investigated for different enzymes[22,32,73]. The rate of plastein formation was determined from the increment in the fraction precipitated in a 10% solution of trichloroacetic acid along the linear section of the kinetic curve. It was shown that, whereas the optimum in the hydrolytic effect of the enzymes employed is in the pH range from 2 to 11, the optimum for plastein formation using the same enzymes is the pH range between 3 and 7 and for the majority of enzymes between 4 and 6. Thus it was found that the optimum pH for the hydrolysis of α-chymotrypsin is 8.0 and that for plastein formation is 5.3. If the difference between the optimum pH values for plastein formation and hydrolysis is denoted by Δ pH then all the enzymes investigated can be divided into three groups: the pepsin type with $\Delta\,\mathrm{pH} > 0$, the chymotrypsin type with $\Delta\,\mathrm{pH} < 0$, and the papain type with $\mathrm{pH} = 0$. Trypsin, which does not exhibit a plastein-forming activity over the entire pH range, constitutes an exception. The values of Δ pH are as a rule greater for enzymes belonging to the chymotrypsin type.

However, there are data showing that chymotrypsin is most effective in the plastein reaction at pH 7.3.[57] The efficiency of plastein formation was estimated in this case from the weight of the filtered fraction. The cause of this discrepancy between the data of different workers remains obscure. Despite this, the fact that the dependence of the efficiency of plastein formation on pH does not coincide with the corresponding pH dependence of the hydrolysis of proteins for all the enzymes investigated leads to the conclusion that the ionic nature of the substrate is an important factor influencing the formation of plasteins.

6. The Influence of Temperature on Plastein Formation

The study of the influence of temperature on plastein formation showed that the weight of the fraction insoluble in the reaction mixture and in 10% trichloroacetic acid solution increases appreciably up to the enzyme denaturation temperature at 60–65°C [29,33,118,119]. The causes of the change in the yield of the plastein reaction when the temperature is altered are not entirely clear. It has been suggested[118] that it is due to the extremely low free energy of the synthesis of polypeptides in the plastein reaction. In the light of present knowledge about the mechanism of plastein formation and its thermodynamics, this explanation is hardly valid. The reason is most probably that an increase of temperature to 55–60°C entails an increase of the energy of the hydrophobic interactions[82,83] responsible for the formation of the gel in the plastein reaction, which leads to an increase of the amount of the fraction sparingly soluble in water.

7. The Influence of the Ionic Strength of the Solution on Plastein Formation

The ionic strength of the solution can influence plastein formation either by altering the activity of the enzyme employed or by affecting the solubility of plastein and desplacing thereby the equilibrium position in one direction or another. The importance of ionic strength in plastein formation is indicated by the finding that the possibility of the formation of gels has been demonstrated on treating a 4% solution of the pepsin hydrolysate of egg albumin at pH 7.3 with chymotrypsin, provided that the solution contains 26% NaCl.[49] As already stated, without the addition of NaCl, plasteins are not formed at this substrate concentration.

A detailed study of the influence of ionic strength on the rate of plastein formation has been carried out in relation to the formation of plastein from egg albumin obtained with the aid of α-chymotrypsin and neutral bacterial protease resistant to the action of high salt concentration[78]. It has been found that different salts act on plastein formation in different ways at a concentration of 1 M. The strength of their influence increases with increase of the charge of the salt cation. The addition of sodium, potassium and lithium chlorides increases the rate of plastein formation by 10%, while the addition of iron, aluminium, and zinc chlorides to the reaction mixture reduces the rate of the plastein reaction by 80–95%. The dependence of the rate of plastein formation on ionic strength, established with the aid of NaCl when α-chymotrypsin is used, is represented by a curve with two maxima of approximately equal height (20–30%) at ionic strengths of 0.1 and 0.8; after the second maximum, there is a sharp decrease of the rate of plastein formation. When a protease which does not lose its activity in concentrated solutions was used, it was shown that the rate of plastein formation increases with increasing ionic strength and that in 3 M NaCl solution it increases by a factor of 2 relative to the initial value.

These studies, combined with studies of the dependence of the activity α-chymotrypsin on the solubility of the plasteins obtained in NaCl solutions at different concentrations, suggest that ionic strength acts on the rate of plastein formation via different mechanisms at different salt concentrations. At low salt concentrations the rate of plastein formation increases owing to the increase of the activity of the enzyme. At high salt concentrations plastein is salted out, which promotes an increase of the rate of its formation, but the enzyme can then lose its activity. If the enzyme does not lose its activity, the rate of the plastein reaction increases; if the enzyme is inactivated, the plastein is formed at a lower rate.

V. INCORPORATION OF VARIOUS AMINOACIDS IN PLASTEINS

The problem of the possible alteration of the aminoacid composition of high-molecular-weight fraction of plasteins in a desired direction has been studied on a fairly wide scale[12,42,52,60,61,63,70,71,100,120-124]. The possibility of increasing the content of all the essential aminoacids in the high-molecular-weight fraction relative to their content in the initial protein was demonstrated. The enrichment can occur on both laboratory and semi-industrial scales[120]. It has been shown that free aminoacids are virtually not incorporated in plasteins[42,52,100,121]. For the successful introduction of a particular aminoacid into a plastein, it is necessary to use aminoacid derivatives. The data in Table 11 show that the amount of the high-molecular-weight fraction of plasteins does not change when different enzymes are used for their synthesis, but the menthionine content in the resulting plastein depends significantly on the enzyme employed. Evidently different methionine derivatives have significantly different abilities to increase the content of this aminoacid in a plastein. Methionine is not incorporated at all if the amino-group is protected by the acetyl group. The incorporation of methionine into a plastein takes place somewhat more successfully if methionineamide is used as the source of the aminoacid.

Table 11. Efficiency of plastein formation and of the incorporation of methionine into plasteins synthesised with the aid of various enzymes using different sources of methionine*.

Enzyme	Yield of plastein reaction	Methionine content in the plastein fraction investigated (in wt.%) after addition of the following methionine derivatives into reaction mixture:				
		Met	AcMet	$MetNH_2$	MetOEt	Met—Met
—	—	1.15	1.44	1.57	2.10	1.50
Ficin	71.68	1.05	1.47	1.32	—	—
Molsin	68.30	1.18	1.53	2.09	3.87	2.70
Nagarse	75.00	1.20	1.22	3.12	7.22	5.10
Papain	78.20	1.15	1.32	1.43	—	—
Pronase	70.10	1.25	1.22	1.25	1.23	1.27
—	—					

*The yield of plastein was determined relative to the non-dialysable fraction of the total mixture by weight.

This shows that the amino-group of the incorporated aminoacid is directly involved in the reaction when methionine is incorporated into a plastein. The methionine content in the plastein increases appreciably when dimethionine and particularly the ethyl ester of methionine are used as the source of methionine. This shows that, although the carboxy-group of the aminoacid is not directly involved in the reaction, its preservation in an active form is essential for the successful incorporation of methionine in a plastein.

From the practical point of view, the possibility of enriching the high-molecular-weight fraction of plasteins in glutamic acid is of considerable interest[123]. Studies have been undertaken on the comparative efficiencies of various glutamic acid esters as a source of glutamic acid in the plastein reaction catalysed by papain[42]. The results of the investigations are presented in Table 12, which shows that the glutamic acid content in the high-molecular-weight plastein fraction can be greatly increased by employing the hydrophobic α,γ-diethyl ester as the source of the aminoacid. The hydrophobic nature of the diethyl ester is almost the same as that of leucine[12].

Table 12. Comparative efficiencies of the employment of various glutamic acid esters as sources of glutamic acid in the plastein reaction catalysed by papain[12]*.

L-Glutamic acid and its esters	Yield, wt.%		Glutamic acid content, wt.%
	w.r.t. hydrolysate	w.r.t. substrate	
Glu-α,γ-OEt_2	95.7	63.8	41.93
Glu-α-OEt	54.3	36.3	32.18
Glu-γ-OEt	58.1	38.7	25.34
Glu	56.9	37.9	25.00
—	60.0	60.0	24.81

*Hydrolysate = pepsin hydrolysate of soya-bean protein; substrate = 2 : 1 mixture (by weight) of hydrolysate and glutamic acid derivative.

In order to investigate the enrichment in lysine of the plastein derived from the pepsin hydrolysate of gluten, synthesised with the aid of papain, a study was made of the influence of the ratio of the weight concentrations of the ethyl ester of lysine and the gluten hydrolysate on the effectiveness of the incorporation of lysine in the plastein. It was found that the maximum degree of incorporation of lysine is reached for a 1 : 2 ratio of the concentrations of the ethyl ester of lysine and the gluten hydrolysate[19]. Similar studies on the enrichment of plasteins in other aminoacids have not been made, but in most investigations the above ratio of the weight concentrations of the aminoacid ester and the protein hydrolysate was in fact used.

A study was made of the dependence of the rate and degree of incorporation of various aminoacids, added to the reaction mixture as aliphatic alcohol ethers of various structure, in plasteins whose formation was catalysed by papain[19,70]. It was found that, when use was made of derivatives of aminoacids with respect to which papain is non-specific (glycine, alanine), the amount of aminoacid ethyl ester incorporated in the plastein increases linearly with the plastein formation reaction time in the presence of the aminoacid ester, amounting to 20% of the total quantity of ester employed in the reaction after 6 h. When the ethyl esters of aminoacids to which papain is specific (L-α-aminobutyric acid, norvaline, norleucine) are used, the incorporation of the aminoacids under virtually the same conditions terminates 2 h after the start of plastein formation; under these conditions, between 50 and 80% of the initial amount of the aminoacid ester is involved in the reaction. The degree of plastein formation after 2 h is only 50%. A distinct correlation has been found between the hydrophobic properties of the side chain of the aminoacids and the rate of their incorporation in the plastein when their ether esters are used. The degree of incorporation of glutamic acid, employed in the form of its diether ester, is the same as for norleucine. Aminoacids branched in the β-position (valine and isoleucine) constitute an exception. For a successful incorporation of the aminoacid, the alcohol with which it is esterified must have an unbranched structure. This requirement is particularly important when aminoacids with respect to

which papain is non-specific are incorporated. The incorporation of any aminoacid is faster the longer the aliphatic chain of the alcohol esterifying the aminoacid. Methionine is linked to the plastein polypeptide chains via peptide bonds[122] and this does not entail the formation of sections of chains consisting exclusively of methionine residues. D-Aminoacids are never incorporated in the plastein.

Thus the structure of the side chain of aminoacids influences primarily the degree and rate of their incorporation in the plastein. The structure of the alcohol esterifying the aminoacid has a smaller influence. The following remarks may be made concerning the mechanism of the incorporation of methionine. Analysis of the terminal amino-groups of the plastein molecules enriched in methionine showed that the methionine residue is located mainly close to the *C*-end of the polypeptide chain of the plastein molecule[61,122]. A three-stage mechanism of the catalysis, involving the formation of an acyl derivative of the enzyme, may be regarded as demonstrated for papain[125]. In this case the similarity of the distribution of methionine residues suggests that the incorporation of methionine in the polypeptide chain involves the formation of a peptidyl derivative of the enzyme, which undergoes nucleophilic attack by the amino-group of the esterified methionine with liberation of free papain and the elongation of the chain by one methionine residue. Subsequently the alcohol molecule is split off and the process can be repeated. Esterification of the carboxy-group promotes in this instance the enhancement of the nucleophilic properties of the methionine amino-group. Any modification of the carboxy-group, for example, the conversion of methionine into the amide of the formation of a dipeptide, has a similar influence on the reactivity of the methionine amino-group, but alcoholic groups are readily split off, which permits the repetition of the process. An alternative mechanism involves the formation of methionine-papain and nucleophilic attack by the peptide amino-group.

The first mechanism, involving the formation of a peptidyl derivative of the enzyme, is supported also by the distribution of the methionine residues preferentially at the *C*-end of the peptide chains and the absence of the incorporation of methionine in the chain when methionine derivatives with a protected amino-group are used as a source of methionine. The same mechanism of the addition of methionine is also supported by the finding that no free methionine, which would have been formed inevitably as a result of the hydrolysis of methionine-papain, has been

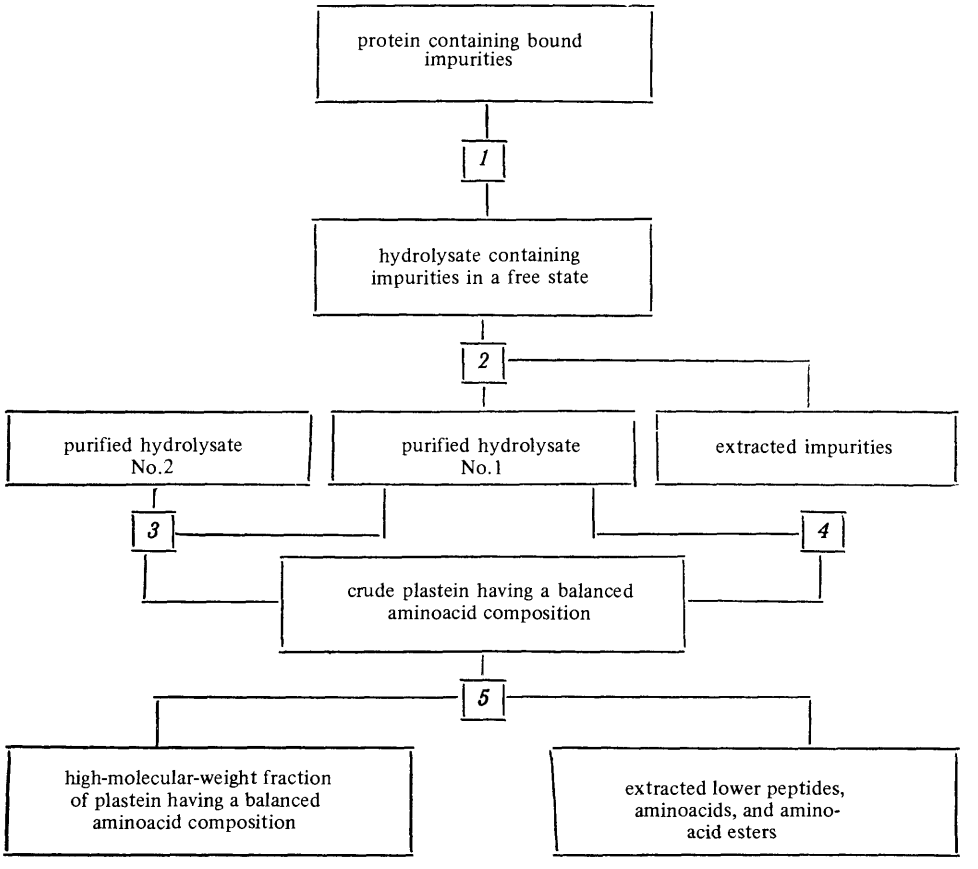


Figure 1. Synthesis of a plastein having a balanced amino-acid composition. Numerals 1 - 5 denote the following operation; 1) hydrolysis by endopeptidases; 2) treatment with organic solvents; 3) addition of endopeptidase; 4) addition of esters of essential aminoacids and endopeptidase; 5) treatment with aqueous ethanol.

found in the reaction mixture. If the reaction mechanism involving the formation of a peptidyl derivative of the enzyme is valid, the observed differences between the rates of incorporation of various aminoacids used in the form of their esters can be attributed to the differences between the binding of different parts of the aminoacid ester molecule to the subcentres S_1 for the aminoacid side chain and S_2 for the alcohol chain[125,128].

Studies on the mechanism of the incorporation of other aminoacids in plasteins under the influence of other enzymes have not been made. One can only postulate, on the basis of general information about the mechanism of the action of endopeptidases[107-111,113,125], that the mechanism of incorporation in such cases is analogous to that examined above. One should note that in many instances a mechanism involving the acylation of the enzyme by the aminoacid derivative is extremely probable. This is indicated by the appreciable incorporation in a plastein of phenylalanine and lysine when the latter are used in the form of ethyl esters with a protected amino-group[52,63,121].

In the enrichment of plasteins by aminoacids side reactions were noted solely in the enrichment of plasteins in lysine catalysed by papain[63]. An appreciable amount of lysine, dilysine, trilysine, and the ethyl ester of dilysine was detected in the reaction mixture only $1\frac{1}{2}$ h after the start of the reaction.

VI. THE USE OF PLASTEINS IN NUTRITION

1. Purification of Proteins and the Preparation of Protein Products with the Required Aminoacid Composition

Numerous studies[19,42,52,60,61,63,70-72,100,120-122,129-132] have shown that protein products with a high food value can be obtained with the aid of the plastein reaction from proteins containing toxic and other undesirable impurities or an unbalanced aminoacid composition. The content of aminoacids in the plasteins obtained is close to ideality under these conditions[1,2]. A scheme for the process is illustrated in Fig. 1. Naturally, protein products with a balanced aminoacid composition can be obtained by simply mixing in definite proportions proteins which are unbalanced with respect to different aminoacids. However, such proteins are by no means always available in a pure form. It is much simpler to purify the hydrolysates than the initial proteins, because the impurities in proteins are incorporated in a network of polypeptide chains. The use of enzymatic protein hydrolysates in food is difficult, because they have a bitter taste and the employment of solid protein products is more customary for man. The main aim of the use of the plastein reaction in this instance is therefore to obtain with its aid protein-like substances from purified hydrolysates. Furthermore, it is naturally important that the enrichment should be by aminoacids synthesised chemically, the latter being introduced into the mixture in the form of ethyl esters.

Studies have shown that plasteins do not have toxic or other undesirable properties and that their nutrient properties are at any rate not inferior to those of the initial proteins and those of plasteins enriched in essential aminoacids are actually superior[72].

Protein-like products with a reduced content of any aminoacid, for example phenylalanine, can be obtained with the aid of the plastein reaction[124,129]. The use of such protein products is the only way of providing protein to persons suffering from phenylketonuria. A scheme for the preparation of plasteins with a low content of phenylalanine is present in Fig. 2. Successive hydrolysis with pepsin and pronase § was essential to ensure that aromatic aminoacids were present in the hydrolysate in a free state. It was found that it is possible to select gel filtration conditions under which aromatic aminoacids are removed from solution almost quantitatively. In order to restore in the resulting plasteins the required levels of tyrosine and tryptophan, the reaction mixture was treated, before plastein formation, with the ethyl esters of the above aminoacids. The subsequent operations involve the purification and more complete isolation of the plastein. As a result of the above process, the phenylalanine content is reduced from 4-5% to 0.05-0.20%, while the content of all the remaining essential aminoacids remains high.

2. Elimination of the Bitter Taste from Enzymatic Hydrolysates

As already mentioned, one of the reasons why enzymatic protein hydrolysates cannot be used in food is their bitter taste[97]. The conclusion that bitter peptides are formed in the enzymatic hydrolysis of proteins can probably be regarded as general for all proteins and all endopeptidases. Bitter peptides with various structures have been isolated from the pepsin hydrolysate of soya-bean protein[133-141]. A characteristic feature of these peptides is the presence of the leucine residue at the ends of the molecule, particularly at the C-end. The important role of hydrophobic terminal aminoacids in the generation of the bitter taste of peptides has been generally observed.

In order to eliminate the bitter taste of enzymatic protein hydrolysates, one can use various procedures. When protein hydrolysates are passed through a charcoal column, the bitter peptides are absorbed preferentially on the charcoal[142]. The bitter taste of enzymatic protein hydrolysate is reduced when the latter are treated with exopeptidases[135,138,139]. However, this method suffers from definite limitations, because, on treatment of the hydrolysates with exopeptidases, free aminoacids are liberated in considerable amounts, which can influence the food value of the hydrolysates.

The plastein reaction proved to be a convenient means for the elimination of the bitter taste from enzymatic protein hydrolysates. It has been found that, when the bitter hydrolysates are used as substrates of the plastein reaction, the resulting products are tasteless[59,97,133,143]. It has been shown that the disappearance of the bitter taste in the plastein reaction is associated with the formation of longer peptides in which the bitter peptides are constituents[73]. Enzymatic hydrolysis of plasteins results in the reappearance of the bitter taste.

The influence of an increased content of glutamic acid on the taste of enzymatic hydrolysates and plasteins is of interest. Plasteins enriched in glutamic acid have no taste, like ordinary plasteins. However, if plasteins with an increased glutamic acid content are hydrolysed by endopeptidases, the bitter taste does not reappear[42,60]. Such a hydrolysate contains peptides of three types: basic, neutral, and acid. The peptides of the first two types are bitter, while those of the third type have no taste. If the tasteless peptides are mixed with peptides of the first two types (jointly or separately), the bitter taste vanishes[42].

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§ Alkaline bacterial protease from *Streptomyces griseus*.

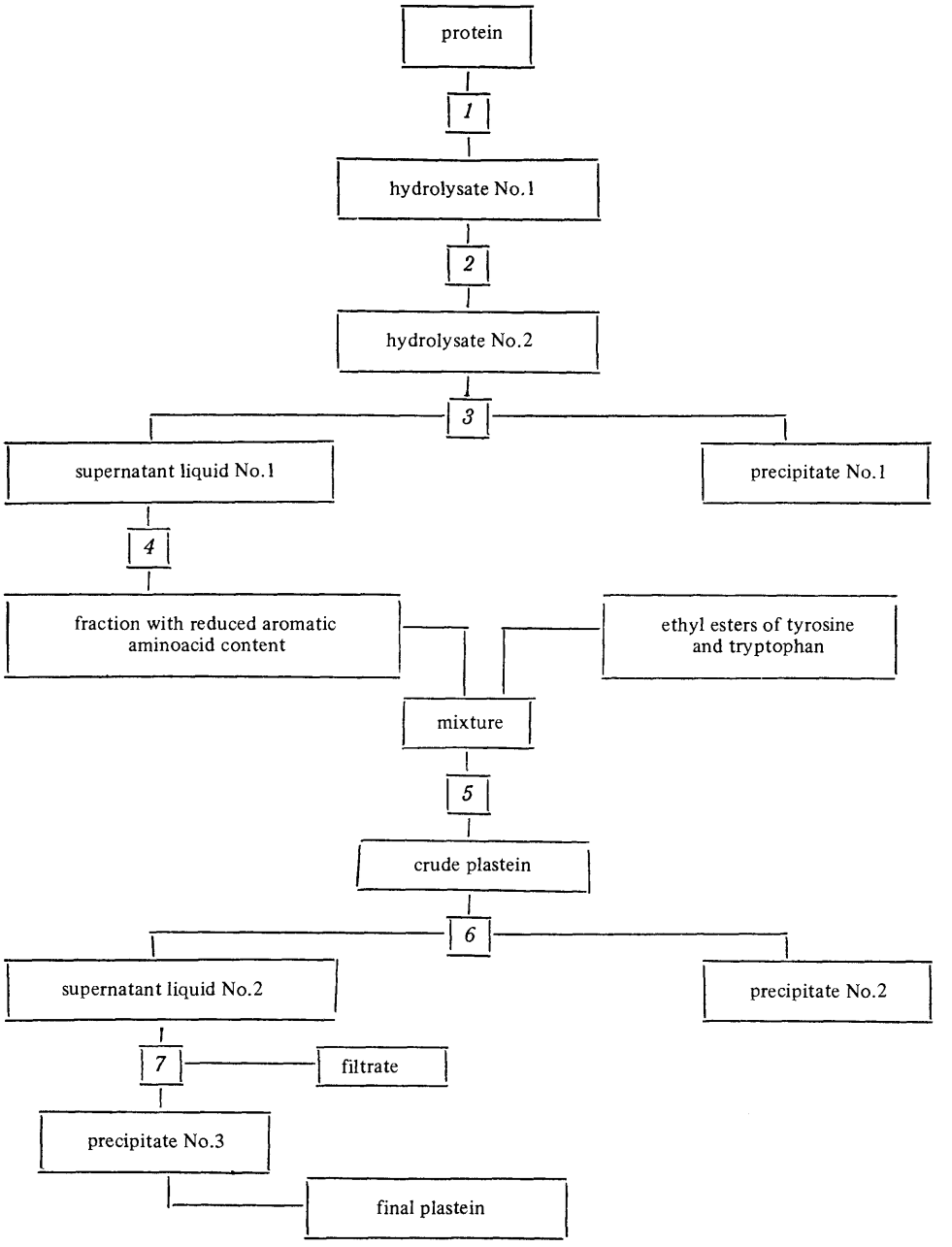


Figure 2. Synthesis of a plastein with a low phenylalanine content. Numerals 1–7 denote the following operations: 1) hydrolysis with pepsin; 2) hydrolysis with pronase; 3) centrifugation; 4) gel filtration; 5) synthesis with papain; 6) centrifugation; 7) ultrafiltration.

The principal component of the peptides of the first type is diglutamic acid. It has been found that diglutamic acid is capable of masking the bitter taste not only of peptides but also of other bitter substances such as $MgCl_2$, caffein, phenylthiourea, and brucine[130]. Consequently in this case the bitter taste disappears as a result of the masking activity of diglutamic acid and not as a result of the formation of new peptides.

Thus the plastein reaction can be useful not only for the preparation of protein-like substances with a high food value from proteins with an unbalanced aminoacid composition but also in the preparation of tasteless enzymatic protein hydrolysates from bitter hydrolysates.

3. Preparation of Protein Pastes and Gels with a High Food Value for Use as Fillers and as Products with an Independent Nutrient Value

The possibility of using plasteins in this way arises from their suitable rheological properties. The problem of the nutrient value of such protein pastes and gels was examined above.

4. Preparation of Mixtures of Peptides with a Particular Smell, Taste, and Other Characteristics for use as Food Additives and Flavours

As already mentioned, plasteins are usually tasteless. It has been shown that enzymatic hydrolysates of plasteins enriched in glutamic acid have the smell and taste of meat[42]. One cannot rule out the possibility that, under certain conditions, one can obtain plasteins or their hydrolysates with any other smell, or taste, but systematic studies on this problem have not been made.

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Summarising the studies carried out in the field of plastein formation, the following points must be noted. The principal practical applications of plasteins have now been outlined. It has been shown that with their aid one can use in food proteins derived from non-traditional sources and chemically synthesised aminoacids. However, the mechanism of the plastein reaction has so far been established only in a very broad outline. The determination of the mechanism of plastein formation is of interest not only from the theoretical but also from the practical point of view, because this can lead to new ways for the preparation and application of plasteins, which will increase the raw material base of the food industry.

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Dynamics of Elementary Processes in Liquids

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The dynamics and mechanism of the basis elementary processes in a liquid have been examined, and their characteristic times (in the range 10^{-13}-10^{-6} s) compared. The relationship between these processes and their influence on the kinetics of chemical reactions has been discussed. The bibliography contains 120 references.

CONTENTS

I.	Dynamics of vibrational relaxation	913
II.	Rotational molecular motion	916
III.	Dynamics of translational motion	922
IV.	Molecular dynamics of pairs	923
V.	Dynamics of van der Waals molecules	925
VI.	Processes of complex formation and solvation	927
VII.	Influence of molecular dynamics on the kinetics of chemical reactions	929

I. DYNAMICS OF VIBRATIONAL RELAXATION

Information on the dynamics of the relaxation of vibrational energy in a liquid is obtained by analysing the line widths in the Raman and infrared absorption spectra or from molecular-acoustic ultrasonic absorption data. In the first case, a significant contribution to the line width is made by the rotational motion of the molecules; the procedure for taking account of this contribution and distinguishing the natural line width (which is determined by the lifetime of the vibrational quantum) is difficult and unreliable. Molecular-acoustic methods are also unreliable, since the absorption of high-frequency sound by the excitation of vibrational degrees of freedom is accompanied by the excitation of conformational transitions in molecules. For this reason, only data obtained for conformationally rigid molecules can be accepted with any confidence. The methods of acoustic and vibrational spectroscopy have established only that the vibrational relaxation times in a liquid lie in the picosecond range [1,2].

Direct measurements of the vibrational relaxation times in a liquid became possible with the appearance of lasers generating powerful single pulses of picosecond duration [3-11]. The principle of the measurement is as follows. A picosecond pulse of frequency ν_L, passing through the liquid being studied, undergoes Raman scattering, exciting intramolecular vibrations with frequency ν_M; the intensity of the scattered Stokes component of the radiation with frequency $\nu_L - \nu_M$ increases as the pulse passes through the substance. The concentration of

vibrationally excited molecules increases simultaneously for each photon of Stokes frequency $\nu_L - \nu_M$ there is one molecule in the first vibrationally excited state $v = 1$. The population of the state $v = 1$ after the passage of the exciting pulse reaches a value of $\sim 10^{-3}$, which is greater by 3–4 orders of magnitude than the thermodynamically equilibrium population. Subsequently, as a result of vibrational relaxation processes $v = 1 \rightarrow v = 0$, the above equilibrium population of the state $v = 1$ disappears with a characteristic time τ_1.

The kinetics of the change in the population of the state $v = 1$ are observed by means of a series of delayed probing picosecond pulses of low intensity and frequency νl. The intensity of the Antistokes component of the radiation with frequency $\nu l + \nu_M$, which is proportional to the population of the vibrationally excited level $v = 1$, is measured. The experimentally measured time corresponding to the decay of the Antistokes radiation is the vibrational relaxation time of the excited molecule.

Experiments of this type are usually carried out using the single picosecond pulse of a neodymium laser, which is divided into two parts. The more powerful part of the pulse passes through a KDP crystal to double the frequency and is used to excite molecular vibrations and Raman scattering in the liquid being studied. The second, weaker part of the pulse passes along a delay line consisting of an echelon—a series of plates of different thickness. The echelon forms a series of probing pulses delayed in time to detect the Antistokes radiation in the molecular vibrations generated by the main (exciting or pumping) pulse. In this version of the experiment, $\nu_L = 2\nu l$. It is also possible to double the frequency of the probing pulses, leaving the frequency of the pumping pulse unchanged, equal to the frequency of the neodymium laser; in this case, $\nu l = 2\nu_L$.

The picosecond pumping pulse ν_L and the Stokes radiation $\nu_L - \nu_M$ generated by it are coherent, so that the vibrational excitation of the molecules is also coherent. In other words, definite phase relationships exist between the vibrations of the excited molecules: they all vibrate in step, in the same phase. The phase synchronism of the vibrations gradually breaks down with a characteristic time τ_2; this leads to the loss of the coherence of the vibrations and the Antistokes radiation and is detected as a change in the coherence of the probing picosecond pulses.

There are thus two relaxation processes: the first characterises the loss of vibrational energy and takes place in a time τ_1; the second characterises the loss of the phase synchronism (coherence) of the vibrations and takes place in a time τ_2. Both are detected by the probing pulses from the intensity of the Antistokes radiation; the non-coherent part of this radiation is used for the former, and the coherent part for the latter. The non-coherent radiation is scattered isotropically and is usually measured at an angle of 90° to the direction of the pumping pulse; the coherent radiation is propagated and detected along the direction of the pumping pulse.

The experimental data on the dynamics of the vibrational relaxation of molecules in the ground electronic state can now be examined. For the N_2 molecule at −196°C with a fundamental vibrational frequency of 2336 cm^{-1}, $\tau_2 = 75 \pm 8$ picosecond (ps),[4] which agrees with the value 79 ± 8 ps found by analysing the width of the Raman line[12]. For the C–Cl symmetric stretch with frequency 459 cm^{-1} in CCl_4, $\tau_2 = 4 \pm 0.5$ ps,[13] which also coincides with the value 4 ps obtained from the Raman spectra. Thus the vibrational relaxation times measured from the Raman spectra are in fact the phase relaxation times.

The dynamics of the vibrational relaxation of the totally symmetric stretches of the CH_3 groups in CH_3-CCl_3 (frequency 2939 cm^{-1}) and in CH_3CH_2OH (frequency 2928 cm^{-1}) have been studied[14] at 300 K. With increase in the delay time of the probing pulses, the intensity of the Antistokes scattering increases at first, reaches a maximum, and then decreases exponentially (Fig. 1). The increase in intensity is due to pumping, and the decrease is due to vibrational relaxation. The coherent radiation decays much more rapidly than the non-coherent radiation: $\tau_1 = 5.2$ ps, $\tau_2 = 1.3$ ps (for CH_3CCl_3); $\tau_1 = 22$ ps, $\tau_2 = 0.26$ ps (for CH_3CH_2OH). Thus the ratios τ_1/τ_2 are 4 and 80 in CH_3CCl_3 and CH_3CH_2OH respectively. For N_2 in liquid nitrogen, $\tau_1 \simeq 1$ s, and the ratio τ_1/τ_2 is even greater ($\sim 10^{10}$).[15] This value is anomalously high; for most vibrations of polyatomic molecules studied in a liquid at room temperature, τ_1/τ_2 has values in the range 10–100.[5]

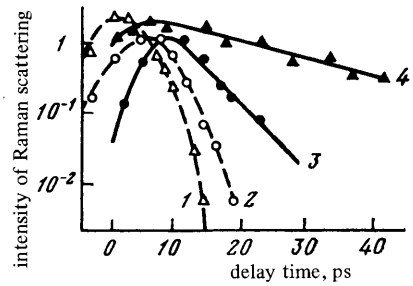


Figure 1. Kinetics of the phase (*1*, *2*) and energy (*3*, *4*) relaxation of the CH_3 stretching vibrations in CH_3CCl_3 (*2*, *3*) and in CH_3CH_2OH (*1*, *4*).[14]

This marked difference in the rates of the phase and energy relaxation is due to the difference in their physical mechanisms. Phase relaxation (loss of coherence of the excited vibrations) takes place as a result of the resonance transfer of a vibrational quantum from an excited to a non-excited molecule. Since the phases of the vibrations of the non-excited molecules are arbitrary and random, this transfer of vibrational energy is accompanied by phase correlation losses, that is loss of coherence. The vibrational quantum does not disappear, but is merely transferred from one molecule to another; its disappearance, that is its transfer to external degrees of freedom of the molecule, is a much slower process. Thus the times τ_2 and τ_1 characterise respectively the kinetics of the processes of the resonance transfer of vibrational energy and its relaxation into the lattice.

The results of experiments which show how the energy relaxation takes place can now be discussed. The energy of the stretching vibrations of the C–H bond correspond to a frequency $\nu_H \simeq 3000$ cm^{-1}, and the energy of the bending vibrations corresponds to a frequency $\delta_H \simeq 1500$ cm^{-1}, that is to half the energy of the stretching vibrations.

The simultaneous measurement of the kinetics of the population of the vibrationally excited states with frequencies 3000 cm^{-1} and 1500 cm^{-1} for the CH_3CCl_3 molecule have shown that excitation of the 3000 cm^{-1} vibration is accompanied by excitation of the 1500 cm^{-1} vibrations.

This means that the population of the excited levels of the bending vibrations takes place through the excited levels of the stretching vibrations. In other words, the relaxation of the 3000 cm^{-1} vibrational quantum takes place by its "exchange" for 1500 cm^{-1} vibrational quanta; the efficiency of this exchange is close to unity[16].

An even more illustrative example is provided by the CH_3CH_2OH molecule[17], which has 21 normal vibrations, five of them in the range 2972–2877 cm^{-1}. The picosecond pumping pulse excited the stretching vibration at 2928 cm^{-1}, and the probing pulses detected the Antistokes scattering on levels in the band 2830–3000 cm^{-1}. It was found that the excitation spectrum was fairly broad (~150 cm^{-1}) and covered almost the entire band of the levels 2830–3000 cm^{-1}. Excitation of the 1550 cm^{-1} and 1350 cm^{-1} levels, which correspond to bending vibrations in the first and second vibrational levels respectively, was also detected.

These results show that the excitation of one stretching vibration (at 2928 cm^{-1}) is very rapidly (in 0.5–1 ps) redistributed between closely situated vibrational levels (in the band 2830–3000 cm^{-1}). It is then transferred slowly (in 22 ps) to vibrational levels of the bending vibrations; from these levels the energy undergoes relaxation into the lattice even more slowly (in ~40 ps).[17]

Data[18] on the excitation of the stretching vibrations of the C–H bonds in hydrocarbons in a band of width 140 cm^{-1} close to 2900 cm^{-1} agree with these conclusions; the relaxation of the population of the excited vibrations was measured. The results are given in Table 1. If τ is normalised to the relative number of methyl groups in the molecule, the values of τ_{norm} obtained remain surprisingly constant in the hydrocarbon series (in particular, in n-heptane there are two methyl groups and seven carbon atoms, so that τ_{norm} = (11.0 ps. 2/7) = 31.14 ps).

Table 1. Vibrational relaxation times in hydrocarbons[18].

Compound	°C	τ, ps	τ_{norm}, ps
n-Heptane	20	11.0	3.14
	−25	14.0	
	−70	16.0	
n-Decane	20	16.0	3.20
	−25	21.0	
Isodecane	20	10.8	3.24
n-Tridecane	20	21.0	3.23
n-Pentadecane	20	24.5	3.27
Hept-1-ene	20	21 0	3.00
Dec-1-ene	20	33.5	3.35
Hepta-1,6-diene	20	60.0	—

This regular feature can be regarded as a consequence of the fact that the vibrational energy rapidly undergoes intramolecular redistribution and is lost through the methyl groups (preferentially through two quanta of the 1450 cm^{-1} bending vibrations).

Data on the transfer of vibrational energy between different molecules can now be examined. Laubereau and coworkers[16] studied relaxation in CH_3CCl_3 + CD_3OD mixtures. On excitation of the stretching vibrations ν(C–H) 3000 cm^{-1} in CH_3CCl_3, it was found that the vibrations ν(C–D) ≃ 2200 cm^{-1} of the CD_3OD molecule are excited, that is intermolecular transfer of a vibrational quantum takes place. Its efficiency depends on the composition of the mixture; the transfer of energy requires the interaction of three particles: an excited CH_3CCl_3 molecule, a non-excited CH_3CCl_3 molecule, and a non-excited CD_3OD molecule. It is assumed that this complex interaction is required in order to establish quasi-resonance conditions for the transfer of energy, since ν(C–H) ≃ ν(C–D) + ν(C–Cl). To satisfy this condition, however, the bimolecular interaction CH_3CCl_3 + CD_3OD is sufficient, since the excess vibrational quantum, equal to ν(C–H) − ν(C–D) may undergo intramolecular transfer to a C–Cl bond of the original CH_3CCl_3 molecule excited in the C–H vibration. A role in the transfer of the vibrational quantum may be played by the bimolecular interaction of the excited CH_3CCl_3 molecule with a van der Waals molecule (CH_3CCl_3 + CD_3OD) (for van der Waals molecules see part V).

In a mixture of CH_3CCl_3 and CD_3OD (60 : 40), the transfer of energy to CD_3OD takes place with $\tau_1 \simeq 13$ ps and with a probability of 0.5; the other half of the vibrational energy of CH_3CCl_3 undergoes intramolecular relaxation through the bending vibrations of the CH_3 group.

In CH_3CCl_3 + CCl_4 mixtures with mole fractions of CH_3CCl_3 (x) equal to 1, 0.8, 0.6, and 0.4, the relaxation time of the vibration ν(C–H) ≃ 3000 cm^{-1} in CH_3CCl_3 increases from 5.2 ps to 29 ps according to the law $\tau^{-1} \sim x^2$ with decrease in x from 1 to 0.4;[16] that is in this case the relaxation of the vibrational energy is a termolecular process: one excited CH_3CCl_3 molecule interacts with two non-excited molecules; the CCl_4 molecules are inert and do not take part in the vibrational relaxation, since the vibrational quantum of the C–Cl bond ($\lesssim$800 cm^{-1}) is small compared with the quantum being relaxed (~3000 cm^{-1}). In this case the relaxation of the energy possibly involves the van der Waals molecule (CH_3CCl_3 + CH_3CCl_3).

The lifetime of the vibrationally excited level of benzene with frequency 991 cm^{-1} (a totally symmetric vibration) is 5 ps, and increases to 8 ps when benzene is diluted with deuterobenzene[19].

The dynamics of vibrational relaxation in electronically excited states of molecules can now be examined. The fluorescence of Rhodamine 6G is delayed relative to an exciting laser pulse[20,21]. The delay is due to the fact that the exciting pulse populates high-lying vibrational levels of an excited singlet state of the molecule, and the fluorescence takes place from the ground vibrational level. These two events—excitation and fluorescence—are separated by a time interval τ, during which the vibrational relaxation of the excited singlet takes place, that is the molecule "descends" from the excited vibrational levels into the ground vibrational level of the electronically excited singlet state.

Quantitative measurements of τ have been carried out for several molecules[22]. A picosecond pulse of frequency ν_L excited the Rhodamine 6G molecule into high vibrational levels of the excited singlet, after which the probing picosecond pulses detected the intensity of the fluorescence from lower-lying vibrational levels at a frequency $\nu_l < \nu_L$ (ν_l usually coincided with the frequency of the centre of the fluorescence band). Thus an inverted population of the vibrational levels of the excited singlet is first created, after which vibrational relaxation restores the normal distribution of the populations; the kinetics of the restoration are detected from the increase in the intensity of the probing picosecond pulses with the passage of time. For Rhodamine 6G in ethanol, the restoration time (that is the vibrational relaxation time in the excited singlet) was 8.3 ps.[22] For the molecules of Erythrocin B, this time was much smaller ($\tau < 2$ ps) and could not be measured[23]. For the molecule of azulene, excited into vibrational levels

lying ~5000 cm^{-1} above the ground level, relaxation to the ground vibrational level takes place with a characteristic time of 7.4 ps;[24] for the vibrational levels lying 500 cm^{-1} above the ground level, this time is 4 ps.[25]

Thus vibrational relaxation in electronically excited states of molecules takes place in a time comparable with or slightly shorter than the vibrational relaxation time of the molecules in the ground electronic state.

II. ROTATIONAL MOLECULAR MOTION

Both physicists and chemists have carried out extensive and successful studies of the rotational–orientational dynamics of molecules in a liquid. Only the most fundamental results will be examined here: 1) the relationship between molecular rotation and the macro-properties of a liquid (in particular, the macro-viscosity); 2) the way in which rotation and reorientation of the molecules take place, and models of this motion; 3) the problem of whether there is a correlation between the rotational and translational motion, and the nature of their relationship; 4) the reorientation of the vector of the angular momentum of rotation; 5) and 6) the quantitative scale of the rotational frequencies.

Before discussing these questions, the physical phenomena on which methods for studying rotational motion are based can be examined. The thermal motion of the molecules in a liquid produces fluctuations in the anisotropy of the polarisability, when the molecules in a small element of volume are randomly found in identical orientations. This fluctuation represents the optical non-uniformity on which scattering of light takes place. Since the fluctuations themselves are oriented randomly, the vectors of their polarisabilities are also directed randomly; this means that the scattered light will be depolarised. The creation and disappearance of fluctuations in the anisotropy take place as a result of the orientational–rotational movements of the molecules, so that the scattered light will be modulated by the frequency of these movements; information on the frequency of the modulation is obtained from an analysis of the line shape in the scattering of the depolarised light. This phenomenon is known as Rayleigh light scattering[26].

Another optical method for studying the rotation of molecules is based on the depolarisation of fluorescence. If isotropically distributed molecules are excited by linearly polarised light, only those molecules will be excited which are oriented in such a way that the dipole moment of their optical transition is directed along the vector of the electric field of the exciting light. Thus the electronically excited molecules have a non-uniform distribution of orientations. If the molecules were stationary, the emission of the fluorescence would have the same polarisation as the exciting light. Molecular rotation, however, leads to random distribution of the orientations of the excited molecules and to depolarisation of the fluorescence. The degree of depolarisation is directly related to the frequency of the molecular rotation.

Both stationary and pulse methods of magnetic radio-frequency spectroscopy (EPR and NMR) are widely used to study rotational dynamics in a liquid. Information on the dynamics is obtained from an analysis of the EPR or NMR line widths and from the electronic or nuclear relaxation times. Both the line widths and the magnetic relaxation times are determined by the intramolecular dipole or quadrupole interactions, the magnitude of which depends on the orientation of the molecule or radical in the magnetic field. Molecular rotation changes the orientations of the particles and modulates the extent of the magnetic interactions; in other words, the molecular rotation modulates the magnitude and direction of the local magnetic fields acting on the electron or nucleus. The line widths and relaxation times depend on the magnitude of the magnetic interactions and the frequency of their fluctuations; if the magnitude of the interaction is known (this is usually the case), the experimentally measured line widths or relaxation times are used to calculate the characteristic times of the rotational–orientational movements.

Mention may also be made of the classical methods of dielectric relaxation, which measure the reorientation times of the electric dipoles of the molecules, and also the methods of Raman light scattering and infrared (vibrational) spectroscopy. In the last two cases, information on the dynamics of rotation is obtained from an analysis of the width of the line and its wings. Finally, the new methods of picosecond spectroscopy may be mentioned.

The questions listed at the start of this section can now be discussed.

1. Relationship Between Molecular Rotation and the Macro-properties of a Liquid

The coefficient of rotational diffusion D_{rot} is determined by the classical relationship

$$D_{rot} = kT/\xi, \tag{1}$$

where ξ is the coefficient of friction experienced by the rotating molecule. In the Debye theory of dielectric relaxation, the coefficient of friction for spherical molecules was calculated from the equations of classical hydrodynamics[27,28]:

$$\xi = 8\pi\eta a^3, \tag{2}$$

where a is the radius of the rotating particle, and η the viscosity of the medium.

On the other hand, molecular rotation is a random stochastic process; it follows from the theory of these processes that the characteristic time of rotational reorientation τ_θ is related to D_{rot} by the following expression:

$$\tau_\theta = (6D_{rot})^{-1}. \tag{3}$$

Substitution of Eqns. (1) and (2) in Eqn. (2) gives the familiar Debye–Stokes–Einstein relationship

$$\tau_\theta = \frac{V\eta}{kT}, \tag{4}$$

which establishes the relationship between the rotational reorientation time of the molecules and the macroscopic viscosity of the medium. This approach was later extended by Perrin[29] to the rotation of ellipsoidal molecules.

A large number of studies have established reliably that the linear relationship between τ_θ and η/T, predicted by this expression, is always observed, but the volumes of the molecules V calculated in this way often do not agree with the actual dimensions of the molecules. In other words, Eqn. (4) gives unsatisfactory quantitative results. Thus depolarised Rayleigh light scattering for the molecules of benzene, toluene, and xylene in different isotropic non-solvating solvents showed[30] that τ_θ obeys the equation

$$\tau_\theta = C\eta + \tau_0, \tag{5}$$

where the constant C was smaller by a factor of 2–6 than that predicted by Eqn.(4); the value of τ_θ, as expected, is close to the period of rotation of the free classical rotator τ_R:

$$\tau_\theta \simeq \tau_R = \frac{2\pi}{9}(I/kT)^{1/2}. \quad (6)$$

In the great majority of cases, Eqn.(4) predicts values of τ_θ which are greater by an order of magnitude than the experimental values. Moreover, the activation energies of rotation (E_θ) are also frequently found to be smaller than the activation energies of the viscosity (E_η), although Eqn.(4) predicts that $E_\theta = E_\eta + RT$. Finally, Eqn.(4) predicts that the dependence on the hydrostatic pressure should be the same for τ_θ and η, whereas the experimentally measured relationships are different [31].

Eqns.(2) and (4) were derived from the equations of classical hydrodynamics for a sphere of volume V, rotating in a continuous medium; clearly, they do not take account of the molecular structure of the liquid, so that in principle it cannot be required that Eqn.(4) give the rotational dynamics quantitatively. In order to "adapt" Eqn.(4) for a correct description of the experimental results, the concept of micro-viscosity η^* was introduced. The quantity η^* is related to the macro-viscosity by the expression $\eta^* = f\eta$, where the coefficient f is a correction for the micro-viscosity. Gierer and Wirtuz [32], in the quasi-stationary approximation, calculated the rotational moments acting on a rotating molecule of radius a from neighbouring molecules of radius b, and determined the coefficient

$$f = \left[6\left(\frac{b}{a}\right) + \left(1 + \frac{b}{a}\right)^{-3}\right]^{-1}. \quad (7)$$

In the simplest case, $b = a$, so that $f = 0.16$; in general, $f \leq 0.16$ (for example, for benzene, dioxan, and cyclohexane, $f \simeq 0.06-0.08$). [32] The correction for the micro-viscosity is introduced semi-empirically, and must be determined experimentally for each rotating molecule–solvent pair.

Considerable progress was made by Steele [33], who developed a theory for calculating the coefficient of friction not from hydrodynamics but at a molecular-kinetic level. It is assumed that the particle moves under the influence of a randomly fluctuating rotational moment; the fluctuations are due to the angular dependence of the intermolecular potential. Since the intermolecular potential of a particle in the environment created by its neighbours is in general anisotropic, the coefficient of friction ξ in Eqn.(1) becomes a tensor quantity; the calculation of the components of the tensor in terms of the parameters of the intermolecular potential is a complex unsolved problem. For the particular case of molecules of the spherical top type, Steele [33] obtained the expression

$$\xi_{ii}^2 = \frac{2I}{\pi}\left\langle \frac{\partial^2 W(R, \Psi)}{\partial \psi_i^2} \right\rangle, \quad (8)$$

where ξ_{ii} is a component of the tensor ξ, I the moment of inertia, and $W(R, \Psi)$ the potential, which is a function of the distance and the angle; the averaging is carried out over all the other variables; in the laboratory system of coordinates, $i = x, y, z$. Eqn.(8) shows that the principal components of the tensor ξ (ξ_{xx}, ξ_{yy}, ξ_{zz}) are proportional to the second derivative of the intermolecular potential with respect to the angle of rotation about the chosen axis.

In recent years there has been a new approach to the calculation of τ_θ within the framework of hydrodynamics [34]. In the derivation of Eqn.(4) it was assumed that the sphere rotates in the continuous medium together with the boundary layer; in other words, it was assumed that the sphere is rigidly bonded to the boundary layer. In fact, this condition is not necessary: the particle may slip relative to the boundary layer. This is equivalent to a decrease in the coefficient of friction and a decrease in τ_θ. The same approach was also deveoped for calculating the coefficient of friction for the rotation of ellipsoids [34] and molecules of arbitrary shape [36]. In particular, for a symmetrical ellipsoid

$$\xi_{xx}^* = \frac{32\pi\eta a^3}{25} e^2 \left(1 - \frac{74}{25} e\right), \quad (9)$$

where a is the length of the semi-axes x and y, and c the length of the semi-axis z; $e = (a/c)^2 - 1$. Fig.2 shows that the ratio ξ_{xx}^*/ξ_{xx} depends on the form of the ellipsoid; here ξ_{xx}^* is determined by Eqn.(9) in the model involving slip, and ξ_{xx} is calculated from the Perrin equations in the hydrodynamic model (without slip). It can be seen that the differences in the coefficients of friction in these two models depend to a marked extent on the shape of the molecules. For an ideal spherical molecule ($a/c = 1$), the model involving slip gives $\xi_{xx} = 0$, that is it predicts free rotation.

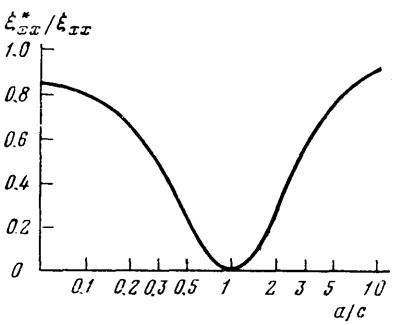


Figure 2. Plot of ξ_{xx}^*/ξ_{xx} against a/c. [37]

This result agrees with Steele's theory: if the intermolecular potential is spherically symmetrical, it follows that $(\partial W/\partial\psi) = 0$, so that from Eqn.(8) it follows that $\xi_{xx} = 0$. In actual fact, molecules with an ideally symmetrical spherical potential do not exist, although many real molecules (CH_4, CCl_4, etc.) have a potential which is almost symmetrical, so that their rotation is restricted to only a slight extent. The hydrogen molecules also undergoes free rotation about the axis directed along the H–H bond, since $\xi_{HH} \simeq 0$. Bauer and coworkers [38] compared the experimental $\tau_\theta(\eta)$ relationships obtained for different molecules by Rayleigh light scattering and NMR relaxation with the theoretical values. It was found that the model including slip reproduces the experimental $\tau_\theta(\eta)$ relationships with good accuracy (±20%).

An interesting feature is that the best agreement is obtained in systems in which there are no solvation effects. In systems where there is strong solvation (for example strong hydrogen bonds), the experimental results are best reproduced by Eqn.(4), that is by the model with rigid binding. Physically, this tendency is wholly reasonable: clearly, solvation will not influence molecular rotation if the lifetime of the complex (or coordination solvate sphere)

is much smaller than τ_θ. On the contrary, stable complexes will rotate as a whole. The dimers of carboxylic acids rotate as a whole in CCl_4;[39] on the other hand, t-butyl alcohol does not influence τ_θ for nitrobenzene[40], since complex formation in this system is weak.

EPR and NMR have been used[41] to study the rotational dynamics of the complex of the stable nitroxide radical with chloroform in various alcohols. A correction for the micro-viscosity was introduced experimentally, and it was shown that the comparatively stable radical–chloroform complex pairs rotate in alcohol as a whole, and the calculated volumes of the rotating particles correspond to their geometric dimensions.

The hydrodynamic model of rotation with slip describes satisfactorily not only the viscosity relationships $\tau_\theta(\eta)$ but also the temperature dependence $\tau_\theta(T)$. As a rule, in systems with slip, $\epsilon_{rot} < \epsilon_\eta$, whereas in systems without slip, $\epsilon_{rot} \simeq \epsilon_\eta$.

2. Models of the Rotation of Molecules in a Liquid

The orientational–rotational movement of a molecule is accompanied by a change in the angular orientation of its axes. It may be assumed that in a time τ_θ the change in the angle is θ; this change may take place either by continuous slow rotation or by a single instantaneous abrupt rotation through an angle θ. Thus in principle it is possible to picture two models of molecular rotation: Brownian diffusion, when the reorientation of the axis of the molecule takes place continuously and randomly, and discontinuous abrupt large-amplitude diffusion. Brownian rotational diffusion can also be regarded as a continuous sequence of abrupt movements of infinitely small amplitude; the difference between the two models of the motion then reduces to a difference in the amplitudes of the elementary abrupt rotational movements.

It is not difficult to understand the physical mechanism of Brownian diffusion (even within the framework of hydrodynamic ideas); it is more difficult to determine the causes and mechanism of abrupt movements of large amplitude. One mechanism[42] assumes that a molecule in a liquid rotates only at those moments when a random fluctuation gives a sufficiently large free volume around it; at these moments the movement of the molecule is regarded as the rotation of a free rotator. When the fluctuation in the free volume disappears, the environment around the molecule contracts, and it remains until the next fluctuation. Theoretical analysis of this mechanism leads to a number of conclusions. Firstly, the activation energy of the rotation must be close to the work of forming the fluctuation of the free volume; this is usually a small quantity, smaller than the activation energy of the viscosity. Secondly, since the rotating molecule is regarded as a free rotator, τ_θ in this model should depend on the moment of inertia of the molecule, so that for isotopically substituted molecules, an isotopic effect in τ_θ should be observed. Atkins and coworkers[42] found that the ratio of τ_θ for the ND_3 and NH_3 molecules is 20% greater than that expected from Eqn.(4); the ratio $\tau_\theta(ND_3)/\tau_\theta(NH_3)$ was found to be close to the ratio $[I_\perp(ND_3)/I_\perp(NH_3)]^{1/2}$, where $I_\perp$ is the component of the moment of inertia perpendicular to the axis of symmetry of the molecule. This is the isotope effect predicted by the theory.

Another mechanism[43,44] assumes that the immediate environment of the molecule has the structure of the crystal lattice, so that the molecule may undergo a reorientation of large amplitude only with the condition that a structural defect or vacancy is created around it, as a result of the displacement of one of the neighbouring molecules into an adjacent lattice site. In this theory, the activation energy of rotation includes the work of formation of the vacancy, and the volume of activation includes the volume of activation for translational diffusion. The first quantity should be close to the molar heat of volatilisation, and the second should be close to the molar volume of the vacancy. The experimentally determined values of these quantities are respectively only 17% of the molar heat of volatilisation and 26% of the molar volume of the vacancy.

Thus the model of the fluctuating free volume shows better agreement with experiment; as will be seen later, this model is also confirmed by the pressure dependence of τ_θ.

How is it possible to establish whether the particle is rotating by a Brownian diffusion mechanism or in abrupt movements? Before answering this question, it is necessary to consider the determination of the coefficient of rotational diffusion D_{rot}.

Eqn.(3) represents a particular definition of D_{rot}; in the general case,

$$D_{rot} = 1/l(l+1)\tau_\theta. \qquad (10)$$

The quantity D_{rot} is a universal characteristic, and is determined by the properties of the rotating particle–medium system; D_{rot} is independent of the physical method of measuring τ_θ. Different methods measure different values of τ_θ, however, and therefore correspond to different values of l (see later).

This important question must be dealt with briefly. All physical methods (mentioned at the start of this section) measure the time dependence of some interaction; usually, the interaction is a random function of time, and its time dependence is described by introducing a correlation function, which characterises the rate at which the "memory" of the magnitude of the initial interaction is lost. It is usually assumed that the correlation function decreases exponentially with a characteristic time τ_θ. In other words, τ_θ is the time in which the magnitude of the interaction changes by a factor of e as a result of molecular rotation. It may be assumed that in this time the "memory" of the magnitude of the initial interaction is lost, that is the correlation disappears; for this reason, τ_θ is called the correlation time of the rotational motion.

The correlation function is expressed in terms of special functions—spherical harmonics of rank l. For interactions of the vector type, $l = 1$; these include the interaction of a constant dipole electric moment with an electric field. For interactions of the tensor type, $l = 2$; these include the dipolar interaction of the nuclei (in NMR), electron–nuclear dipolar interaction (in EPR), and polarisability (in Rayleigh light scattering). Eqn.(3) is obtained from Eqn.(10) for $l = 2$; for dielectric relaxation, $l = 1$ and $\tau_\theta = (2D_{rot})^{-1}$.

From the definition (10) it now follows immediately that for Brownian diffusion

$$\tau_\theta(l=1)/\tau_\theta(l=2) = 3\ . \qquad (11)$$

In other words, if τ_θ is measured in a given system by two different methods, the ratio of τ_θ obtained should be equal to 3. One of the methods should measure an interaction of the vector type (for example from the dielectric relaxation or from an analysis of line shape in the infrared vibrational spectrum), and the other method should use an interaction of the tensor type (for example EPR, NMR, or Rayleigh or Raman light scattering).

The physical significance of Eqn.(11) is that in the rotation of the molecule, the tensor interaction changes more rapidly, so that the change in this interaction takes place e times more rapidly, in a shorter time τ_θ.

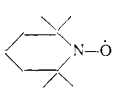
If the molecule rotates in abrupt movements with an amplitude which is sufficiently large for any interaction to change by a factor of not less than e, it follows that in this case τ_θ will be independent of the physical method of measurement; in this case

$$\tau_\theta(l = 1)/\tau_\theta(l = 2) = 1 . \qquad (12)$$

Eqn.(11) is applicable for Brownian diffusion, and Eqn.(12) for diffusion by abrupt movements; by determining the ratio $\tau_\theta(l = 1)/\tau_\theta(l = 2)$ experimentally, it is possible to reach conclusions regarding the mechanism of rotational diffusion. This approach, and a rigorous theory, were developed by Valiev and Ivanov[45].

The mechanism by which rotation of the molecule takes place can now be examined. Gershon and coworkers[46] determined τ_θ by Rayleigh light scattering in a number of liquids, and compared the results with the dielectric relaxation times. It was found that in quinoline, nitrobenzene, chlorobenzene, aniline, and pyridine at 25°C, the ratio of these times is close to unity. It was therefore concluded that the rotation of the above molecules takes place in abrupt movements with a large amplitude (~1–1.5 radian). On the other hand, the rotation of the molecules of nitrobenzene and camphor in CCl_4 and CS_2 takes place by a diffusion mechanism: for these molecules, the ratio $\tau(l = 1)/\tau(l = 2)$ is 3 ± 0.5.[45]

Recently, particular attention has been paid to the study of the rotation of nitroxide radicals, which are widely used as spin markers and probes[47,48]: the form of their EPR spectrum is sensitive to the model of rotation. It was found that the radical $(SO_3)_2^{2-}NO$ in aqueous glycerol rotates in almost abrupt movements[49], whereas the rotation of the molecule of spin-labelled haemoglobin is more effectively described by a continuous diffusion model[50]. In a study of a number of radicals of different shape and size, Kuznetsov[51] showed that the rotation of small radicals is described more effectively by the model of diffusion by abrupt movements, whereas that of large and unsymmetrical radicals is described more effectively by the continuous diffusion model[51]. For the radical



the conclusion that it undergoes abrupt movements was confirmed by comparing the values of τ_θ obtained from dielectric relaxation and from the EPR spectra[52]; their ratio being close to unity. A general tendency is for large and asymmetric molecules in viscous solutions to rotate by continuous diffusion; small molecules in non-viscous solutions generally rotate by abrupt movements.

In general, in a liquid, rotational movements of different frequency, scale, and amplitude are allowed, but movements of particular frequencies and amplitudes predominate, depending on the viscosity, temperature, size, and shape of the molecules. The movement of large molecules at high viscosities takes place with a low amplitude, and rotation through a large angle is made up of a large number of rotations through small angles; this is the case of continuous diffusion. With decrease in the viscosity, movements with large amplitude begin to predominate, and in the limit these can be regarded as abrupt movements. Situations intermediate between these two limiting cases are possible.

3. Relationship Between Rotational and Translational Motion

Data on the relationship between rotational and translational molecular motion in a liquid can be obtained by NMR relaxation. Studies of this kind have been carried out by Jones and coworkers[31], who studied the pressure dependence of the intramolecular dipole contribution to the relaxation of the protons of the molecules of acetone, benzene, chlorobenzene, toluene, and other derivatives of benzene, dissolved in the corresponding deuterated compounds. The intramolecular dipole contribution to the nuclear relaxation is determined only by the rotation of the molecules, and its pressure dependence shows unambiguously that the rotation depends on pressure.

The proton relaxation times of acetone and benzene are independent of pressure up to pressures of several kilobars. This means that the freezing of the translational mobility of the molecules at high pressures does not influence their rotational mobility, that is the rotation of these molecules is autonomous and independent of their translation. The physical cause lies in the fact that in these molecules the main contribution to the nuclear relaxation is made by rotations of the methyl groups (in acetone) and rotation of the benzene molecules about the C_6 symmetry axis; these movements also take place in the solid.

In substituted benzenes, where the symmetry of rotation is destroyed, the intramolecular dipole contribution to the nuclear relaxation shows a marked pressure dependence. In these molecules, rotation is related to translational motion; the relationship is stronger, the greater the van der Waals radius of the substituent in the aromatic ring.

Thus in the relationship between rotation and translation, the principal role is played by the shape of the molecules: for symmetrical molecules, rotation is practically autonomous, whereas for asymmetric molecules there is a marked correlation between these two types of molecular motion. This conclusion is confirmed by data on the scattering of slow neutrons by the liquid; in this case the theory which does not take account of statistical correlation of rotational and translational motion provides a poor description of the experimental data[53].

The correlation of the rotational and translational motion is quite natural; for a given molecule to rotate, it is necessary to have a fluctuation of the free volume around it, and this fluctuation is impossible without rotational–translational movement of its neighbours.

4. Behaviour of the Rotational Moments of Molecules

Exceptionally important information on the dynamics of molecular motion is given by NMR in those cases where the nuclear relaxation takes place as a consequence of spin–rotational coupling. A randomly rotating molecule is a system of moving charges, and therefore creates its own randomly varying electromagnetic field, the magnetic component of which induces the relaxation of the nuclei of the molecule. The correlation time of this spin–rotational coupling is the time corresponding to the change in the angular momentum of the molecule τ_J; in fact, this is the time which is necessary for the molecule to lose the "memory" of its original angular momentum or, in other words, it is the time between the collisions of the molecules in the liquid. The determination of the relationship

between the times τ_θ and τ_J is of particular importance for an understanding of the mechanism of molecular motion.

The behaviour of the angular momentum can be described by two different models[54]. One of these (the J-model) assumes that τ_J is the average time between instantaneous molecular collisions in which there are simultaneous changes in the magnitude and direction of the angular momentum. The other (the M-model) assumes that only the direction of the momentum changes, and that its magnitude (and hence the rotational energy) does not change. The results of the theoretical calculation of τ_J and τ_θ for these models are given in Fig. 3.[55]

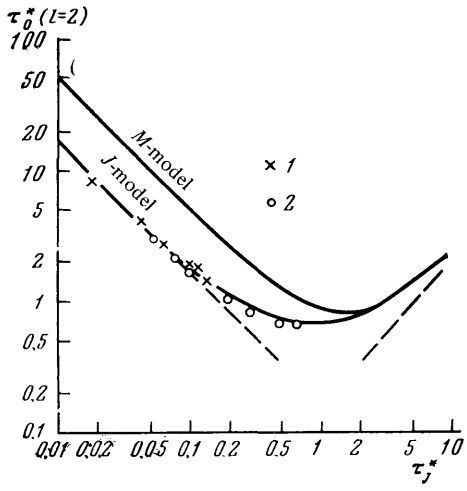


Figure 3. Relationship between τ_θ^* ($l = 2$) and τ_J^* in the J- and M-models[55]. The points give the experimental data: *1*) CS_2 (167–308 K), *2*) ClO_3F (140–368 K); $\tau^* = \tau(kT/I)^{1/2}$.

In the range of Brownian continuous diffusion $\tau_J \ll \tau_\theta$, and they are related by the expressions

$$\tau_J\tau_\theta = I/l(l+1)kT \qquad (13)$$

for the J-model and

$$\tau_J\tau_\theta = 3I/l(l+1)kT \qquad (14)$$

for the M-model (I is the moment of inertia of the molecule). These relationships are also obtained from the Langevin equations for the classical mechanics of a rotator[37]; Eqns. (13) and (14) also lead to the characteristic of Brownian diffusion already discussed [Eqn. (11)].

In the range of diffusion by abrupt movements, Eqns. (13) and (14) no longer apply (as expected), and τ_J is comparable with τ_θ; the physical significance of this result corresponds to the definition of diffusion by abrupt movements. This region lies close to the critical conditions for the existence of the liquid, and in this region the two models (J and M) give similar results. In the gaseous phase, according to kinetic theory, $\tau_\theta \sim \tau_J$ (Fig. 3).

The points in Fig. 3 give the experimental results for the ClO_3F and CS_2 molecules[56,57]. For ClO_3F, the value of τ_θ was determined from the relaxation of ^{35}Cl nuclei, induced by quadrupole coupling ($l = 2$), and τ_J was obtained from the relaxation of ^{19}F nuclei, taking place as a result of spin–rotational coupling[56]. At low temperatures, $\tau_\theta \gg \tau_J$, and Eqn. (13) is fulfilled, that is the rotation of the molecule takes place by the Brownian mechanism; at high temperatures, τ_θ is comparable with τ_J, and rotation takes place by abrupt movements. In CS_2, the relaxation of the ^{13}C nuclei takes place as a result of spin–rotational coupling and the anisotropy of the chemical shift[57]; both contributions have been measured, and the values of τ_θ and τ_J given in Fig. 3 obtained.

Similar measurements of τ_θ and τ_J have been carried out for the molecules of fluorobenzene, fluorine, CF_4, CCl_3F, HCl, SF_6, HBr, PH_3, CH_4, etc.[55] In all cases the J-model is applicable, that is paired collisions of the molecules are accompanied by simultaneous changes in the magnitude and direction of the angular momentum; the actual collisions take place randomly, and are not correlated. The applicability of the J-model confirms the view that there is a high efficiency of exchange of energy between the rotational and translational degrees of freedom.

The temperature dependence of τ_J is of interest. Since increase in temperature leads to an increase in the thermal velocities, it was expected that the time between the collisions of the molecules in the liquid should decrease, that is τ_J should decrease. Experiment reveals the opposite tendency. Thus for liquid fluorine at 56 K (m.p. 53.5 K), $\tau_J = 9.5 \times 10^{-14}$ s and increases with increase in temperature with an activation energy of 300 cal mole^{-1}.[58]

For fluorobenzene, τ_J also increases with increase in temperature, even at a constant density, that is for a constant intermolecular distance (experiments at high pressures)[31]; a similar increase in τ_J has been observed for CF_4, ClO_3F, etc. To explain this phenomenon, it was necessary to assume that the radius of the particles decreases with increase in temperature. In other words, with increase in the kinetic energy of the molecules, the distance of their maximum approach on collision decreases, that is more extensive overlap of the electron clouds of the colliding particles takes place. This corresponds to an increase in the free path of the molecules and hence to an increase in τ_J.

Eqns. (10) and (13) can be used to obtain the equation

$$D_{rot} = \left(\frac{kT}{I}\right)\tau_J, \qquad (15)$$

in which (kT/I) is the square of the angular velocity of the rotation, and τ_J the time between the collisions which lead to a change in the rotational moment and angular velocity.

The results given in Fig. 3 and in Eqns. (13) and (14) are of particular practical importance. They make it possible to estimate the values of D_{rot} and τ_θ from τ_J; τ_J in turn can be estimated from the thermal velocity of the molecules v and from the intermolecular distance d: $\tau_J \simeq dv^{-1}$. Here, $d = \bar{r} - \sigma$, where $\bar{r}$ is the average distance between the centres of the molecules, and σ the diameter of the molecule, which can be found from data on the elastic scattering, from molecular models, or from the molar volume of the solid:

$$\bar{r} = \left(\frac{V\sqrt{2}}{N}\right)^{1/3}; \quad v = \left(\frac{8kT}{\pi m}\right)^{1/2};$$

V is the molar volume of the liquid, and N Avogadro's number. For a molecule of the benzene type, $\sigma \simeq 5.2$ Å, $\bar{r} \simeq 6.0$ Å, $v \simeq 6 \times 10^4$ cm s^{-1}, and $\tau_J \simeq 1 \times 10^{-13}$ s.

5. Anisotropy of the Molecular Rotation

Spherical molecules rotate isotropically, whereas the rotation of non-spherical molecules must be characterised by a rotational diffusion tensor. From the definition (8) of the components of the tensor coefficient of friction it follows that there are two factors responsible for the anisotropy of the rotation: the anisotropy of the force potential $\partial W/\partial\psi$ and the anisotropy of the moment of inertia I, the components of which, I_{xx}, I_{yy}, and I_{zz}, may in general be different.

The axes of symmetry of a molecule usually coincide with the axes of symmetry of its force field and the axes of the tensor of the moment of inertia, so that the principal components of the tensor of the rotational diffusion are the frequencies of rotation about the axes of symmetry. If the molecule has no axes of symmetry, the principal axes of the tensor of the rotational diffusion usually coincide with the principal axes of the tensor of the moment of inertia (with the condition that the molecule is not involved in any strong intermolecular interaction creating a marked anisotropy of the potential; in this case the axes of rotation coincide with the axes of the potential).

In general, rotation must be defined by three correlation times (relative to each of the three axes), but for molecules of the symmetric top type there are only two times, $\tau_{\parallel}$ and $\tau_{\perp}$ (rotation relative to the axis of highest order symmetry and about axes perpendicular to it).

The anisotropy of molecular rotation can be successfully studied using the NMR relaxation of nuclei exhibiting a quadrupole moment; it is necessary that the molecules contain not less than two nuclei which exhibit quadrupole moments and which do not lie on the same molecular axis[59] For example, for the CD_3CN molecule the rotational correlation time calculated from the rate of relaxation of ^{14}N nuclei describes the motion at right angles to the axis of symmetry of the molecule, since the gradient of the electric field inducing the relaxation of the nucleus is directed along the C≡N bond; this time is 1.2 ps. The time 0.14 ps, calculated from the rate of relaxation of the deuterium nucleui, characterises the rotation about all three axes, although the predominant contribution is made by the rotation about the axis of symmetry. Thus for CD_3CN at 25°C, $\tau_{\parallel} = 0.14$ ps, $\tau_{\perp} = 1.2$ ps. The activation energies of rotation about different axes are also different: $\epsilon_{\parallel} = 0.8$ kcal mole^{-1}, $\epsilon_{\perp} = 1.7$ kcal mole^{-1}.[59]

The pressure dependence of $\tau_{\parallel}$ and $\tau_{\perp}$ has been studied [60]; at 23°C, $\tau_{\parallel}$ is almost independent of pressure (up to 2 kbar), whereas $\tau_{\perp}$ increases by a factor of almost 3. The activation volumes are $V_{\parallel} \leq 2$ cm^3 mole^{-1} and $V_{\perp} = 8.5$ cm^3 mole^{-1}; these quantities have the significance of the fluctuations of the free volume required to unfreeze rotation. It is obvious that for rotation about a perpendicular axis it is necessary to create a fluctuation of a large volume, whereas rotation about an axis of symmetry requires almost no additional volume. These results agree with the theoretical models of rotation previously examined.

A similar relationship has been found for CD_3I (at 23°C, $V_{\parallel} < 2$ cm^3 mole^{-1}, $V_{\perp} = 10.0$ cm^3 mole^{-1}), and for toluene and other molecules [31]. The rates of relaxation of the quadrupolar nuclei D and ^{35}Cl have been used to determine $\tau_{\parallel}$ and $\tau_{\perp}$ for $CDCl_3$;[59] at 20°C the values are 1 ps and 2 ps, and the activation energies are 0.8 kcal mole^{-1} and 1.6 kcal mole^{-1} respectively.

For BCl_3, the ratio $\tau_{\perp}/\tau_{\parallel} \simeq 0.75$, and for $VOCl_3$ and CCl_3CN these ratios are 1.4 and 2 respectively (20°C); for pyridine, the value of $\tau_{\perp}/\tau_{\parallel}$ changes considerably with temperature (it is equal to 3 at −20°C and 1 at 90°C).[61] The anisotropy of the rotation of the nitroxide radicals used as spin markers and probes is of considerable interest. The anisotropy of their rotation was first studied by Vasserman and coworkers[62]. The rotation of the radical $(SO_3)_2^{2-}NO$ is anisotropic[49,51,62]: it is most rapid about the axis perpendicular to the N–O bond and the $2p\pi$-orbital of the unpaired electron; the ratio of the frequencies of rotation in water and in glycerol has the values 2.9 and 4.7. The anisotropy of the rotation depends on temperature only for small radicals[51]. The temperature dependence of the anisotropy of rotation is an important characteristic: its existence indicates that the anisotropy of the rotation is due to the anisotropy of the force potential, and its non-existence indicates that the rotational anisotropy is due to the anisotropy of the moment of inertia.

For benzene, toluene, nitrobenzene, and mesitylene, the correlation times $\tau_{\parallel}$ and $\tau_{\perp}$ obey Eqn.(5), but the dependence of these times on the viscosity is strongly anisotropic, that is the proportionality coefficients $C_{\parallel}$ and $C_{\perp}$ differ considerably[63]. This indicates that the simple hydrodynamic model is unsuitable for the description of the mechanism of the elementary movements.

6. Molecular Rotation Frequency Scales

The molecular movements of highest frequency in a liquid are those movements which lead to a change in the moment of inertia; their characteristic times τ_J are of the order of 10^{-13} s or less, and coincide with the times obtained from an analysis of the far edge of the Rayleigh scattering line[64]. If the liquid is regarded as a quasi-crystalline solid, this time can be identified with the period of the oscillations in the lattice sites.

The rotational reorientations of molecules take place much more slowly (see Table 2); even small and symmetrical molecules undergo reorientations in times of ~2–10 ps, and the rotation of large and unsymmetrical molecules in viscous solvents takes place in times of 10^{-10}–10^{-9} s.

Table 2. Rotational correlation times of various molecules in liquids.

Molecule	°C	τ_0, ps	Refs.
HF	25	0.8	65
CS_2	20	2	66
C_6H_6	20	4	61
Cyclopentane	20	1.3	67
ClO_3F	−143÷95	0.06 exp (900 RT)	58
F_2	−217	6.8	65
Bromobenzene	23	13	64
Nitrobenzene	25	32	66
Toluene	20	14	64
m-Nitrotoluene	23	44	64
Rhodamine 6G in octanol	20	1600	68
Rhodamine 6G in $CHCl_3$	20	100	68
Bengal Pink in CH_3OH	20	180	69
Bengal Pink in iso-C_3H_7OH	20	890	69
Eosin in water	20	550	69
Macromolecules (mol.mass ~10^6)	20	~10^8	–

The activation energies of rotation for small and symmetrical molecules are 1–3 kcal mole^{-1}, and for large and anisotropic molecules they may reach 5–7 kcal mole^{-1} and sometimes more. An interesting feature is that the pre-exponential factors for the rotational correlation times amount to ~10^{-13} s and coincide with τ_J.

New possibilities for the study of quantitative dynamics were opened up by picosecond spectroscopy (the data for dyes given at the end of Table 2 were obtained by direct observation of the depolarisation of the fluorescence by picosecond spectroscopy).

The phenomenon of optically induced birefringence (optically induced Kerr effect) is of particular interest. The electric field of a powerful laser pulse passing through the liquid brings about partial orientation of electrically anisotropic molecules. After the passage of the light pulse, the system exhibits the property of birefringence, which disappears with a characteristic time τ_θ. The action of super-fast shutters (Kerr cells) is based on this phenomenon.

III. DYNAMICS OF TRANSLATIONAL MOTION

A macroscopic characteristic of translational dynamics is the diffusion coefficient

$$D_t = \frac{\langle l^2 \rangle}{6\tau}, \qquad (16)$$

where τ is the time in which a particle, on the average, is displaced through a distance l. A familiar expression is the Stokes–Einstein relationship

$$D_t = \frac{kT}{6\pi a\eta}, \qquad (17)$$

which is obtained from the hydrodynamic equations for the movement of a sphere of radius a in a continuous medium with a viscosity η. As in the case of rotational diffusion, this macroscopic description is inadequate; the experimental values of D_t are usually greater than the predicted values, particularly in viscous liquids, polymer solutions, etc. In order to adapt Eqn.(17) for the description of the experimental results, the concept of the micro-viscosity η^* ($\eta^* = f_t\eta$) was introduced [32], with micro-viscosity coefficient

$$f_t = 0.16 + 0.4\,(a/a_L), \qquad (18)$$

where a_L is the radius of the molecules of the solvent. With this correction, Eqn.(17) in most cases reproduces the experimental results satisfactorily (to within 20–30%).

Strictly speaking, Eqn.(17) is not applicable for the description of the micro-dynamics of diffusion. It is often used, however, with the assumption that $\langle l^2 \rangle \simeq \langle a^2 \rangle$ and $\tau = \tau_t$, where τ_t is the time corresponding to a displacement through a distance of the order of the molecular diameter. The particle can cover this distance either by continuous Brownian movement or by abrupt movements.

Existing theories of the molecular mechanism of translational movements are based on the concepts of fluctuations of the free volume and their migration, and in fact represent a development of Frenkel's ideas [70]. The theories predict the Arrhenius temperature dependence of the diffusion coefficient $D = D_0 \exp(-\epsilon_D/RT)$ with ϵ_D close to the activation energy of viscous flow. For some atoms and molecules (of the type Ar, O_2, etc.), however, diffusion takes place without activation, and the diffusion coefficient is proportional to temperature and independent of viscosity [71]. The Arrhenius relationship usually applies in a narrow temperature range; the study of diffusion over a wide temperature range shows that ϵ_D itself depends on temperature. The activation volume of diffusion (which is obtained from the pressure dependence of D) also is not constant and depends on temperature [31]. This indicates that translational molecular movement is not an elementary process, and although different theories give different aspects of this process satisfactorily, there is no complete rigorous theory of both rotational and translational diffusion.

The most extensive information on translational dynamics is obtained by measuring the magnetic relaxation of nuclei and electrons (NMR and EPR). The diffusion coefficients are determined by the spin echo method; the correlation time τ_t and the amplitude of the translational displacement are calculated from the intermolecular dipole contribution to the relaxation of the nuclei (in NMR) or electrons (in EPR).

An example is provided by data [72] on the relaxation times of the protons of chloroform diluted with deuterochloroform. The relaxation time depends on the diffusion coefficient, the distance of closest approach of the nuclei when the molecules come into contact, and the amplitude of the displacement. If the approach distance is taken as 4.1 Å (from molecular models), the amplitude of the displacement is found to be 4.6–5.5 Å. On the other hand, if it is assumed that diffusion takes place by a Brownian mechanism, that is if it is assumed that the amplitude of the displacement is infinitely small, the approach distance is 2.3 Å, which is a physically unrealistic value. From this it may be concluded that translation in chloroform takes place by abrupt movements, with an amplitude of 4.6 to 5.5 Å.

The correlation time τ_t is calculated from the experimentally determined diffusion coefficients using Eqn.(16), where l = 4.6–5.5 Å:

$$\tau_t = 4 \cdot 10^{-13} \exp(-2300/RT).$$

The pre-exponential factor is close to the value of τ_J, and characterises the period of the vibrations of the molecule in the equilibrium position. In liquid HF at 25 °C, it was found that $D = 10^{-4}$ cm^2 s^{-1}, τ_t = 2.3 ps (from NMR data) or 4.0 ps (from neutron scattering); the amplitude l = 3.7 Å (NMR) or ~5 Å (neutron scattering) [65]. For cyclopentane and cyclohexane at 20 °C, the amplitudes of the rotations, calculated from the scattered neutron spectra, are 0.3–0.6 Å (the displacement of a point along the surface of the sphere of rotation); the amplitudes of the vibration of the centre of gravity of the molecules are 1.3–1.9 Å in the temperature range from the melting point to the boiling point [67].

The quasi-elastic scattering of cold (low-energy) neutrons is becoming a powerful experimental method for studying the molecular dynamics of liquids. The energy spectrum of scattered neutrons gives the frequency spectrum of the atomic–molecular movements with characteristic times 10^{-4}–10^{-11} s and amplitudes of the atomic–molecular displacements 0.1–10 Å.

Neutron scattering data show that both the orientational and the translational movements contain as components displacements of both small amplitude and large amplitude. Their relative proportions depend on the shape of the molecules, temperature, and the viscosity of the liquid.

In recent years, fairly exact mathematical methods have been developed for calculating the coefficients of rotational and translational diffusion. These methods are based on the view of a liquid as a system of close-packed rigid spherical (or almost spherical) particles. These

ideas effectively give the static structure of a liquid. It is assumed[73] that they can also be used to describe its dynamics. A dynamic theory has been developed[74], based on the fact that single-particle movement in a liquid is controlled by the forces of intermolecular repulsion (the steep branch of the intermolecular potential). The dynamics of this system are close to the dynamics of a system of rigid particles[74]. It is assumed that the long-range (changing slowly with distance) intermolecular forces can be neglected. This approximation is applicable to the description of single-particle movement, but is naturally inapplicable to the examination of the collective correlated movement of several particles (for example in liquid crystals).

Thus the one-particle approximation works satisfactorily, and makes it possible to calculate the coefficients of rotational and translational diffusion with good accuracy.

Direct proof that the dynamic processes in a liquid are controlled by short-range forces of repulsion has been obtained[75] by calculating the correlation functions for the velocity of particles in a model liquid, in one case taking account of the entire intermolecular Lennard–Jones potential, and in the second case taking account of only its repulsive part; the correlation functions were found to be the same in both cases.

The same method (computer modelling of the dynamic processes) showed that the diffusion coefficients in a model liquid consisting of rigid spheres coincides to within 10 units with the diffusion coefficients in a liquid in which the entire Lennard–Jones potential is taken into account, that is long-range forces of attraction do not play a significant role in the molecular dynamics of a liquid, although these forces play a decisive role in the thermodynamics of liquids.

IV. MOLECULAR DYNAMICS OF PAIRS

All bimolecular chemical and physicochemical processes take place in pairs of interacting particles (chemical reactions, energy transfer, quenching of excited states, complex formation, etc.); the probability that a process will take place in a single encounter of the reacting particles is determined to a considerable extent by the dynamics of the pair. These dynamics can be examined for the case of a pair of radicals; this reproduces all the characteristic features of the behaviour of any molecular pair of uncharged particles.

A radical pair is a dynamic system in which the partners may diffuse into the volume, move apart, and return again to the original pair, undergoing diffusion journeys along random trajectories of different length and duration. The probability of return gradually decreases with increase in the length of the trajectory; this probability will be defined by a function $f(t)$. In other words, $f(t)$ is a function of the distribution of the pairs with respect to lifetime, that is the probability that a pair survives to the instant of time t; this means that the partners leaving a pair at the instant $t = 0$ return again to the pair at the instant t with a probability $f(t)$.

The probability of reaction in a pair (for example recombination) consists of two terms:

$$P = \varepsilon + (1-\varepsilon)\int_0^\infty \varepsilon f(t)\,dt\,. \qquad (19)$$

The first term takes account of primary recombination, which has a probability ϵ; it is due to the "collapse" of those pairs in which the radicals have been unable to move apart before the instant t. The second term expresses the probability of secondary recombination, due to the repeat encounters of radicals which have left the pair at the instant $t = 0$ and returned to it at the instant t.

From the theory of the random diffusion of particles in a liquid[77], the following expression was proposed for the function $f(t)$:

$$f(t) = mt^{-3/2}\exp\left(-\frac{\pi m^2}{p^2 t}\right), \qquad (20)$$

where $p = \int_0^\infty f(t)dt$ is the probability that the pair undergoes at least one secondary encounter ($1 - p$ is the probability that the radicals never return to the original pair); usually, $1/2 < p < 1$. The values of p and m are determined by the following expressions[78]:

$$p \simeq 1 - (1/2 + 3\rho/2\sigma)^{-1}$$
$$m = 1.036\,(1-p^2)\,(\rho/\sigma)^2\,\nu^{-1/2},$$

where ρ is the diameter of the contact pair, σ the step of the mean-square diffusion displacement of the radicals ($\sigma^2 = 6D\nu^{-1}$), and ν the frequency of the diffusion displacements.

The function $f(t)$ in the form of Eqn. (20) describes the molecular dynamics of any pair of neutral particles. Substituting Eqn. (20) in Eqn. (19) gives the probability of reaction in the pair:

$$P = \varepsilon + \varepsilon\,(1-\varepsilon)\,p^{\cdot}. \qquad (21)$$

This equation in fact determines the magnitude of the cage effect. It is applicable with the condition that the lifetime of the isolated radicals is infinite. In fact, the radicals have a finite lifetime: within the diffusion time they may be transformed into other radicals (by decomposition, isomerisation, or replacement). As a result, chemical dynamics are superimposed on the diffusion dynamics of the pair; the function $f(t)$ must be modified in such a way that it takes account of the diffusion trajectories and return of only the surviving radicals. If the rate constant of the chemical transformation is k, the probability of "survivial" of the radicals until time t in the pair is equal to $\exp(-kt)$; the dynamics of a pair of surviving radicals are then described by the function

$$\varphi(t) = f(t)\exp(-kt). \qquad (22)$$

This function describes the dynamics of any pair of particles having a finite lifetime $\tau = k^{-1}$; for processes involving the bimolecular quenching or transfer of energy (vibrational or electronic), k is the rate constant of the radiative or non-radiative unimolecular deactivation of the excited particle. For processes involving radicals, the function (22) describes the dynamics of not only chemical but also physical transformations (inversion, rotation, *cis-trans* isomerisation); it can then be used to calculate the degree of preservation of the stereochemical configuration or optical activity in the product formed.

Substituting the function $\varphi(t)$ in Eqn. (19) in place of $f(t)$ gives

$$P = \varepsilon + \varepsilon\,(1-\varepsilon)\,p\cdot\exp\left[-(2m/p)\sqrt{\pi k}\right]. \qquad (23)$$

For processes involving the recombination of radicals, P is the probability of formation of the product in the radical pair, and ϵ the probability of recombination in each contact of the partner. For preservation of the stereochemical configuration, P is the probability of preservation,

and k the frequency of the inversion or spatial reorientation of the particles in the diffusion journeys. For processes involving excited particles, P is the probability of the quenching or transfer of energy in the pair formed by the excited molecule and the quenching agent (or energy acceptor), and ϵ the probability of this process in each contact of the partners.

The dynamics of radical pairs exhibits another remarkable feature: in addition to diffusion and chemical dynamics, it exhibits spin dynamics, that is the dynamics of the evolution of spin states, or singlet–triplet transitions. Spin dynamics are controlled by the magnetic interactions in the radicals and depend on the difference in the Zeeman energies of the radicals (and hence on the external magnetic field intensity), the energy of the hyperfine electron–nuclear interaction, and the magnitude of nuclear spin of the radicals. This leads to magnetic effects in radical reactions, the importance of which was understood and evaluated only in recent years [79,81]. These include the chemical polarisation of nuclei and electrons, the magnetic isotope effect, and the influence of a magnetic field on chemical reactions [80]; a complete review of studies in this field has been published [82].

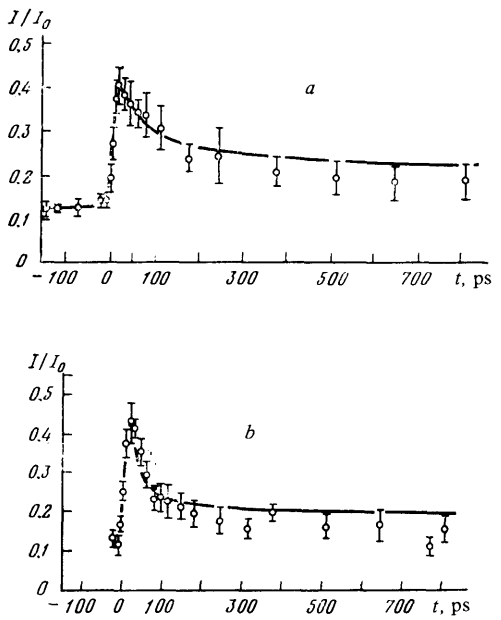


Figure 4. Kinetics of the cage recombination of iodine atoms: *a*) in CCl_4; *b*) in hexadecane [84]. The points give the experimental results, and the lines the results of the calculation using the Noyes model; the moment $t = 0$ corresponds to the end of the exciting pulse.

The dynamics of molecular pairs of free uncharged particles has been discussed; its experimental verification can now be examined.

Firstly, quantitative studies of magnetic effects (in particular, the chemical polarisation of nuclei) have shown that the function $\varphi(t)$ in the form of Eqn.(22) effectively describes the experimental results. The polarisation of nuclei takes place in a pair as a result of singlet–triplet transitions with a characteristic time of $10^{-8}-10^{-10}$ s; the main contribution to the polarisation is therefore made by long diffusion trajectories, the duration of which is comparable with the time of singlet–triplet transitions. In other words, the main contribution to the polarisation of nuclei is made by diffusion displacements with a duration $t \gg m^2/p^2 \simeq 10^{-12}-10^{-11}$ s. With this condition, the function $f(t)$ has the simple form

$$f(t) \simeq mt^{-3/2} \qquad (24)$$

and describes the large-scale diffusion dynamics of long-lived particles.

Secondly, computer calculations of the molecular dynamics of pairs (so-called machine experiments) have confirmed the general form of the function $f(t)$ given by Eqn.(20) and have shown that the probability of a secondary encounter of the particles in a pair decreases with time as $t^{-3/2}$, in agreement with Eqn.(24). [83]

Finally, direct confirmation of the form of the function $f(t)$ has been obtained by picosecond spectroscopy [84]. A solution of I_2 in CCl_4 and $C_{16}H_{34}$ was irradiated by a powerful 5300 Å laser pulse of duration ~5 ps. At this frequency, I_2 is excited into the state $^3\Pi_{0_u^+}$, from which collision-induced predissociation to two atoms in the state $^2P_{3/2}$ takes place. The iodine atoms recombine in the pair (in the cage) or move apart and recombine in diffusion encounters with other atoms, avoiding cage recombination. The formation of I_2 molecules from the atoms is detected by probe laser pulses which measure the transmission at a wavelength absorbed by I_2 (5300 Å); the results are shown in Fig. 4.

After the passage of the exciting pulse, the transmission of the solution at first increases as the I_2 molecules dissociate into atoms, and then decreases, when the iodine atoms begin to recombine, and reaches a stationary value after ~800 ps. The stationary value of the transmission does not coincide with the initial transmission; the difference corresponds to the number of iodine atoms which have avoided cage recombination and moved into the volume. Their recombination in the volume is limited by diffusion, and takes place in a time of $\sim 10^{-8}$ s. The fraction of atoms leaving the cage is 25% in CCl_4, and 5% in hexadecane [84].

The characteristic time of the cage recombination of iodine atoms is ~140 ps in CCl_4, and ~70 ps in hexadecane [84]; this time can in fact be regarded as the lifetime of the cage in the liquid. The kinetics of the recombination are described satisfactorily by Eqn.(20); the best agreement between theory and experiment is obtained for the following values of the parameters: frequency of the abrupt diffusion movements $(1-5) \times 10^{12}$ s^{-1} in CCl_4 and $(2-20) \times 10^{12}$ s^{-1} in $C_{16}H_{34}$; amplitude of the elementary diffusion displacement 0.5–1.0 Å in CCl_4 and ~0.1 Å in $C_{16}H_{34}$. [84] These values are of course approximate, but they give the correct order of magnitude and are physically reasonable.

The function $f(t)$ characterising the dynamics of pairs of oppositely charged particles should describe the diffusion movement of the particles in the Coulombic field of mutual attraction. The problem of the behaviour of a

pair of this kind has been solved in radiation chemistry [85,88], where it is necessary to calculate the probability of the return of a thermalised electron or negative ion to the original positive ion.

Finally, mention may be made of the dynamics of combined pairs, in which the interacting centres are joined by a chain of atoms and chemical bonds. The dynamics of pairs of this kind represents essentially conformational and not diffusion dynamics. If however the connecting chain is sufficiently long, diffusion will influence the rate of the conformational transitions. An example of systems of this kind is provided by nitroxide biradicals, in which two paramagnetic nitroxide fragments are joined in a single molecular system [47]. The exchange interaction of the unpaired electrons in these biradicals takes place chiefly in intramolecular collisions of the paramagnetic centres, so that it depends on the flexibility of the connecting bridges, the number of chemical bonds, and the solvent[87]. The encounter frequency and rate of spin exchange are controlled by the conformational dynamics of the connecting bridge.

A study of the frequency of the intramolecular transfer of an electron between two α-naphthyl groups joined by a polymethylene chain [88] showed that the frequency of transfer decreases according to the law $(n+1)^{3/2}$ for $n \geq 6$ (n is the number of methylene groups in the chain). The activation energy of transfer is small, and independent of n.

The disproportionation of the biradicals

$$\dot{C}H_2-(CH_2)_n-\dot{C}O \rightarrow CH_2=CH-(CH_2)_{n-1}-C\overset{O}{\underset{H}{\diagdown\!\!\diagup}}$$
$$(n = 7-11)$$

is an intramolecular process; the disproportionation product is found to show polarisation of the nuclei, which depends on the magnetic field intensity [80]. The polarisation is produced as a result of $S-T_{-1}$ transitions in the biradical at the moments at which the ends of the biradical, in their random movement, pass through a position in which the condition $2J \simeq g\beta H_0$ is satisfied (when the exchange energy of the electrons is equal to the Zeeman energy). In this position, the energy levels of the singlet (S) and one of the triplet (T_{-1}) states intersect; the magnitude of the polarisation depends on the frequency with which the system passes through this point.

Quantitative calculations of the nuclear polarisation [90] have shown that the probability of passage through the point of intersection of these levels is given satisfactorily by the Treloar function for a freely connected chain.

In both of these examples, the molecular dynamics of the combined pairs is controlled chiefly by the conformational dynamics of the connecting bridges.

V. DYNAMICS OF VAN DER WAALS MOLECULES

Van der Waals molecules (VM) are weakly bonded complexes of atoms, radicals, or molecules, which exist as a result of intermolecular attraction. Dimers of the atoms of the inert gases (Ne_2, Ar_2, Kr_2, Xe_2), and also the complexes $Ne-H_2$, $Ar-H_2$, $Kr-H_2$, $Xe-H_2$, $Ar-N_2$, $Ar-O_2$, $Ar-HF$, $(H_2)_2$, $(O_2)_2$, H_2-N_2, $(NO)_2$, $(CO_2)_2$, etc., are known and have been extensively studied. The properties of VM have been reviewed [91]. Van der Waals molecules have characteristic vibrational–rotational spectra and are detected by infrared and microwave spectroscopy, in experiments on molecular scattering, and in molecular beams.

The main contribution to the energy of formation of VM is made by dispersion interaction (equilibrium distances 3.5–4.5 Å). The dissociation energies of VM are comparable with their kinetic thermal energy and amount to 0.2–0.9 kcal mole^{-1}, so that almost every collision with a foreign molecule leads to decomposition of the VM. At room temperature and a pressure of 1 atm, the time between molecular collisions is $\sim 10^{-10}$ s; the lifetime of the VM is approximately the same. Decrease in temperature increases the lifetime and concentration of VM, and increase in pressure decreases the VM lifetime.

The formation of VM is revealed in the macro-properties of gases, changing the form of the $p-V-T$ diagram, the magnitude of the second virial coefficient, the viscosity, etc. It is assumed [91] that VM take part in processes involving the transfer of its energy, translational–rotational exchange, the spin–rotational relaxation of electronic spin in quantum generators with optical pumping. In addition, VM induce processes of gas condensation; it is suggested [91] that various gaseous chemical reactions may take place with the participation of VM; these reactions may have a negative temperature coefficient (for example the oxidation of NO).

An interesting role is played by VM in reactions taking place in molecular beams. The angular distribution of the reaction products indicates unambiguously that many reactions include the formation of an intermediate complex, the lifetime of which is greater than or comparable to the period of rotation of the complex ($\tau \geq 10^{-12}$ s).[92] This lifetime is much greater than the duration of the collision of the reagent molecules. These reactions include: $Cs + RbCl \rightarrow CsCl + Rb$; $Cl + BrI \rightarrow ClBr + I$; $Cl + I_2 \rightarrow ClI + I$; $D + H_2 \rightarrow DH + H$, etc.[92] The intermediate complexes in these reactions can be regarded as VM, since they can hardly involve any specific interaction other than van der Waals interaction (for example the complex D–H–H, which precedes the reaction $D + H_2 \rightarrow DH + H$).

VM must undoubtedly also exist in a liquid, although their lifetime, other conditions being equal, should be shorter than in the gaseous phase. It is possible to detect VM from the increase in the correlation time of rotational motion in a liquid; the measured time is a complex function of the reorientation time of single molecules and their pairs [93]. This is revealed experimentally by an increase in the rotational correlation time of the molecules with increase in their concentration (at constant viscosity).

These effects are usually investigated by studying the dependence of τ_θ on viscosity at different concentrations of the molecules. The $\tau_\theta(\eta)$ relationship obeys Eqn. (5) at all concentrations, but at η = const. the time τ_θ is greater at higher concentrations of the molecules, that is for a greater contribution of pairs to the measured light scattering. An increase is shown not only by the values of τ_θ but also by their values extrapolated to $\eta = 0$, which are close to the periods of rotation of free rotators in the gaseous phase. This effect has been observed for solutions of benzene, toluene, nitrobenzene, perfluorobenzene, and chloroform [30,40]. Thus for nitrobenzene in an infinitely dilute solution in CCl_4 the time τ_θ is 2.4 ps, and reaches 5.6 ps with increase in the concentration of nitrobenzene to 50% (at the same viscosity). It was concluded that the nitrobenzene molecules are "joined" in pairs in such a way that their planes are arranged in parallel [93]. The pairs of benzene molecules are "joined" with their planes at right angles; the same relative orientation of neighbouring molecules is observed in solid and liquid benzene (from X-ray scattering data [94]). The recently

detected[94] dimers of benzene in the gaseous phase apparently have the same structure, since they exhibit a dipole moment.

The dimers of molecules are short-lived species; their lifetime τ is shorter than the period of rotational reorientation in the liquid τ_θ, but greater than the period of free rotation in the gaseous phase, and amounts to several picoseconds. Thus the dimers can be regarded as van der Waals molecules. The depolarisation of the Rayleigh light scattering in benzene + perfluorobenzene and perfluorobenzene + mesitylene mixtures has revealed pairs of these molecules[95]: the value of τ_θ for the mixtures is 2–4 times τ_θ for the isolated molecules (at a constant viscosity in the same inert solvent, for example in CCl_4). In this case also, the molecular pairs can be regarded as VM with a lifetime $\tau \lesssim \tau_\theta$.

As noted earlier, Rayleigh scattering is observed in solutions of optically anisotropic molecules in optically isotropic solvents. The molecules of these solvents are symmetrical and do not exhibit anisotropy of the polarisability (for example CCl_4). In molecular collisions, however, the electronic structure of the interacting particles changes, with a consequent breakdown of the symmetry of the electron cloud and the production of short-lived fluctuations in the anisotropy of the polarisability. For this reason, symmetrical molecules (and even atoms) also show Rayleigh scattering; the line corresponding to this scattering is usually very broad, and is superimposed on the narrow line corresponding to the ordinary Rayleigh scattering of optically anisotropic molecules.

Rayleigh scattering induced by collisions has been observed in gases (He, Ne, Ar, Xe, H_2); it has been shown that it is due to van der Waals molecules $(He)_2$, $(Ne)_2$, etc.[91] The same scattering has been observed in liquids (Xe, Ar, $SnBr_4$, CCl_4); the correlation times of the paired interactions inducing the Rayleigh scattering amount to 1–3 ps.[96] These times are obviously too long to be regarded as the duration of the collision. In a liquid, the light scattering is most probably due to VM, in which the anisotropy of the optical polarisability is revealed; the lifetime of these VM is ~1–3 ps and is shorter than the period of rotational reorientation.

The problem of possible complex formation by the most important chemical reagent—molecular oxygen—is of particular interest. Evans[97] was the first to observe singlet–triplet absorption by benzene in the presence of oxygen; it was assumed that oxygen removes the spin-forbidden character of the singlet–triplet transition in benzene, and hence interacts somehow with the electron cloud of the benzene molecule. It was later found[98] that in the presence of oxygen, new absorption bands appear in the electronic spectra of hydrocarbons, alcohols, and aromatic molecules; they were assigned to charge-transfer complexes. The equilibrium constants for complex formation were small, however, and the bond energies $\lesssim$300 cal mole^{-1}. The results were often contradictory and indefinite; the formation of the complex $C_6H_6 + (O_2)_2$ was also suggested[98]. A displacement of the $^1\Sigma_g^+ \longleftrightarrow {}^3\Sigma_g^-$ absorption band of molecular oxygen from 760 nm (in the gas) to 630 nm (in water) is also observed[99]. All these facts have been regarded as signs of the interaction of the electron clouds of molecular oxygen and organic molecules

Convincing proof of this interaction was obtained by NMR: in the presence of molecular oxygen, dissolved under a pressure of 3–50 atm in the liquid, the NMR lines of most molecules studied (water, alcohols, dioxan, amines, acetone, cyclohexene, phenylacetylene, chloroform, benzene and its derivatives, anthracene, etc.) undergo paramagnetic shifts and broadening[100,101]. The paramagnetic shifts show unambiguously that in the interaction of the oxygen molecule with dissolved molecules, overlap of their electron clouds and partial transfer of the unpaired electrons of oxygen to the organic molecules take place.

This "collectivisation" of electrons can be regarded as a sign of the participation of oxygen in a complex, but the equilibrium constants of complex formation are very small and do not exceed 10^{-2} litre mole^{-1}.[101] The bond energies in the complex are also small, and different for different groups of a given molecule. Thus the bond energy measured from the temperature dependence of the paramagnetic shift of the protons of the CH_3 group in toluene is 1.7 kcal mole^{-1}, whereas that measured from the protons of the aromatic ring is close to zero; in methanol, the bond energy measured from the protons of the CH_3 group is close to zero, whereas that measured from the hydroxyl protons is 0.5 kcal mole^{-1}.[101] Thus different fragments of the same molecule interact in different ways with oxygen.

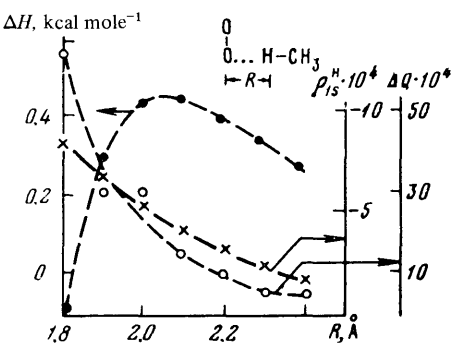


Figure 5. Dependence of ΔH, ρ^H_{1S}, and ΔQ on the distance between the partners of the complex $O_2 \ldots CH_4$.

In binary or ternary mixtures, the paramagnetic shifts depend little or not at all on the composition of the mixtures; this means that there is practically no competition between different molecules for a position in the coordination sphere of oxygen[101]. All these facts show that oxygen forms very weak complexes, which must be regarded as van der Waals molecules. Some results of a quantum-chemical calculation of the most stable configuration of the system $O_2 + CH_4$ are given in Fig. 5; the calculated equilibrium distance is ~2.05 Å, the bond energy $\Delta H \simeq 400$ cal mole^{-1}; the charge ΔQ transferred from oxygen to the methane molecule is $\sim 2 \times 10^{-3}$; the spin density ρH_S on the hydrogen atom attached to the p_z orbital of oxygen is $\sim 3 \times 10^{-4}$. The calculated values of the bond energy and the transferred spin density are close to the experimental values.

The equilibrium constant (~10^{-2} litre mole^{-1}) can be used to estimate the lifetime of VM involving oxygen: the value is ~10^{-12} s. The paramagnetic broadening of NMR lines is completely determined by the intermolecular contribution[101]; the intramolecular contribution, due to the dipole electron–nuclear interaction within the VM, is

negligible. This means that the lifetime of the VM is shorter than the period of its rotational reorientation, that is $\tau \leqslant (1-5) \times 10^{-12}$ s.

In general it should be noted that it is almost impossible to distinguish a distinct boundary between van der Waals molecules and weak short-lived complexes. Neither the lifetime nor the bond energy nor even the transfer of spin (electron) density can serve as unambiguous criterion of the difference between these particles. The only difference between a complex and a VM is the nature of the forces holding the partners in the complex or in the van der Waals molecule; it is fairly difficult, however, to detect this difference experimentally. The partners in VM are held by van der Waals (mainly dispersion) forces; in contrast to the case of the forces responsible for specific interactions in a complex, it should be impossible to saturate dispersion forces; in other words, the coordination number for VM may be large (up to 4–6). It is impossible in practice, however, to reach the concentration range in which this characteristic feature of VM might be detected.

VI. PROCESSES OF COMPLEX FORMATION AND SOLVATION

Complex formation by particles is generally accompanied by the partial overlap of the electron clouds of the partners, which changes the reactivity of the particles in the complex. In the study of complex formation by organic molecules in a liquid, the following principal problems arise: what types of complex exist, what orbitals are used by the partners for complex formation, in what combinations are these orbitals used, how are the orbitals oriented in space, what are the interatomic distances in the complexes, and what are the lifetimes of the complexes? Extensive information on complexes has been obtained by the classical methods of optical spectroscopy, NMR, and dielectric measurements [102]. In recent years, NMR studies of paramagnetic complexes of the type $\dot{R}\ldots L$ (where $\dot{R}$ is an organic radical, and L an organic ligand molecule) [47] have revealed a number of important regular features of complex formation. An advantage of complexes of the type $\dot{R}\ldots L$ is that they have an unpaired electron, which is situated in collectivised molecular orbitals of the complexes. The unpaired electron is transferred with a definite probability (measured by NMR) to the ligand atoms, and reflects all the interactions taking place in the complex.

The theory of the paramagnetic shifts and broadening of the NMR lines in paramagnetic complexes has been developed, the dependence of these spectral changes on the concentration of the complexes in the solution studied, and an approach to the extraction of information on the structure and dynamics of these complexes formulated [103-105]. The basic idea behind this approach is to organise competition between different ligand molecules for the orbitals of the radical. Thus for example the paramagnetic fragment of a nitroxide radical (Fig. 6) uses its π- and n-orbitals for complex formation with the ligand. If the solution contains two types of ligand, one of which reacts using the π-orbital while the other reacts using the n-orbital, the paramagnetic shifts of each of these ligands will be independent of the concentration of the other. Each ligand may add on independently to different orbitals of the radical, forming a two-coordinated complex. In this case there is no competition between the ligands for the orbitals of the radical. On the other hand, if both ligands add on to the same orbital of the radical forming complexes of the same type, the mole fractions of the complexes with each of these ligands (and hence their paramagnetic shifts) will depend on the concentration of the corresponding ligand. In this case the ligands compete for the same orbital of the radical.

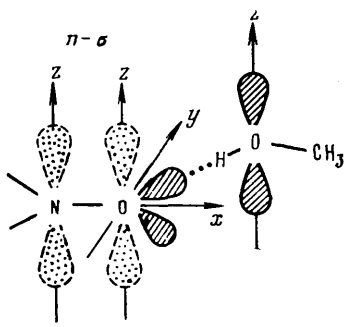


Figure 6. Participation of the orbitals of the paramagnetic fragment of a nitroxide radical in the formation of $n-\sigma$ complexes.

Table 3. Ligands competing with solvent molecules for the orbitals of a radical [105].

Ligand	Functional group (atoms to which the NMR signal relates)	Solvent	Type of complex	K, litre mole^{-1}	ρ_{1s}^{H} or ρ_{2s}^{13C}*
H_2O	OH (protons)	C_6H_5OH	$n-\sigma$	0.7	$1\cdot10^{-3}$
$CHCl_3$	CH (protons)	CH_3OH	$n-\sigma$	0.6	$0.8\cdot10^{-3}$
$(CH_3)_3CNH_2$	NH_2 (protons)	CH_3OH	$n-\sigma$	—	—
	CH_3 (^{13}C)	C_6H_{12}	$\pi-\sigma$	0.1	$1.3\cdot10^{-4}$
CCl_4	CCl (^{13}C)	C_6H_{12}	$\pi-n$	0.5	$1.8\cdot10^{-3}$
C_6H_{12}	CH_2 (^{13}C)	CCl_4	$\pi-\sigma$	0.05	$2.6\cdot10^{-4}$
$H_3CCH_2CH_2-C\equiv$	CH_3, CH_2 (^{13}C)	C_6H_{12}	$\pi-\sigma$	—	—
$H_3CCH_2CH_2-C\equiv$					

*ρ_{1s}^{H} is the spin density in the 1s orbital of the hydrogen atom forming the hydrogen bond; ρ_{2s}^{13C} is the spin density in the 2s orbital of the carbon atom.

This principle has been widely used to determine the structures of the complexes of nitroxide radicals [105]; the chief results of the experimental studies are summarised in Tables 3 and 4.

Molecules containing hydroxyl or amino-groups form complexes of the $n-\sigma$ type; in these, the radical provides a n-orbital, to which the σ-bond O–H (or N–H) of the ligand is attached (see Fig. 6). These are ordinary hydrogen-bonded complexes; the ligands forming the hydrogen bond (H_2O, alcohols, amines, chloroform, organic acids, etc.) compete with one another for the n-orbital of the radical (Table 3). The hydrogen bond joins the radical and the ligand with the formation of a single quasi-π-system, in which ~1% of the density of the unpaired electron is transferred to the π-orbital of the ligand; this spin density subsequently extends to the ligand atoms by a

hyperconjugation or spin polarisation mechanism, leading to the appearance of spin density of different sign in the σ-electronic system of the ligand[106]. Various properties of complexes of radicals with a hydrogen bond are given in Table 5.

Table 4. Ligands not competing with solvent molecules for the orbitals of a radical[105].

Ligand	Functional group (atoms to which the NMR signal relates)	Solvent	Type of complex	K, litre mole^{-1}	ρ_{1S}^{H*}
CH_3OH	OH (protons)	CCl_4, C_6H_{12}	$n-\sigma$	3	$1\cdot10^{-3}$
C_2H_5OH	OH (protons)	CCl_4, C_6H_{12}	$n-\sigma$	0.7	$0.7\cdot10^{-3}$
$(CH_3)_3CNH_2$	NH_2 (protons)	C_6H_{12}	$n-\sigma$	—	—
$CHCl_3$	CH (protons)	CCl_4	$n-\sigma$	0.6	$0.8\cdot10^{-3}$
$C_6H_5OCH_3$	CH_3 (^{13}C)	CH_3OH	$\pi-\sigma$	—	—

*See footnote to Table 3.

Table 5. Equilibrium constants K, lifetimes τ_l, distances $r_{O\ldots H}$, and spin densities ρ_{1S}^{H} on the hydrogen atoms in complexes.

Ligand	K, litre mole^{-1}	τ_l, s	$r_{O\ldots H}$, Å	$\rho_{1S}^{H}\cdot10^3$
CH_3OH	3.5	$4\cdot10^{-11}$	1.75	−9.6
$CHCl_3$	0.6	$2.6\cdot10^{-11}$	1.77	−7.7
$C_6H_{11}OH$	—	$1.1\cdot10^{-10}$	1.45	−1.75
$(CH_2OH)_2$	—	$3\cdot10^{-11}$	1.74	−8.2

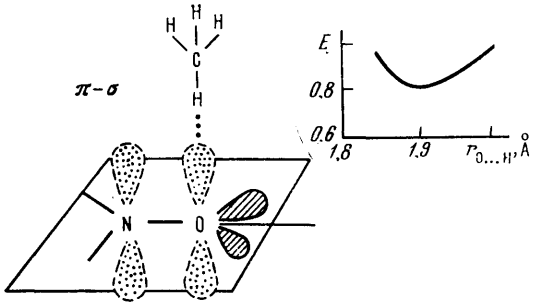


Figure 7. Molecular model of the $\pi-\sigma$ complex of methane and the potential energy curve for the complex; the spin density on the hydrogen atom of the ligand, attached to the π-orbital of the radical, is 3×10^{-4}, and that on the 2*s* orbital of the carbon atom is 1×10^{-3}.

Complexes of the $\pi-\sigma$ and $\pi-n$ type are of particular interest; they are formed using the π-orbital of the unpaired electron and the σ-bond C−H ($\pi-\sigma$ complexes) or with the participation of the unshared pairs of the ligands ($\pi-n$ complexes). The first are formed with saturated hydrocarbons using the CH_2 or CH_3 groups and are detected from the paramagnetic shifts of the ^{13}C nuclei[105]; a model of such a complex is shown in Fig. 7.

The $\pi-\sigma$ complex obviously lies on the reaction coordinate for the transfer of a hydrogen atom and precedes the activated complex, so that the distribution of the spin density and the mechanism of its propagation in $\pi-\sigma$ complexes is of theoretical interest.

Molecules forming complexes of the $\pi-n$ type compete with molecules forming $\pi-\sigma$ complexes for the π-orbital of the radical (see Tables 3 and 4). They do not compete, however, with molecules forming $n-\sigma$ complexes. The $\pi-\sigma$ and $\pi-n$ complexes are generally much less stable than the $n-\sigma$ complexes; their equilibrium constants and lifetimes are an order of magnitude smaller than those for $n-\sigma$ complexes. They are not van der Waals molecules, however, since their formation involves rigorously defined localised interactions: each partner provides its own particular orbitals, which exhibit regular relative orientations and arrangements.

If the molecule contains different functional groups, they may take part in the formation of different complexes. Thus t-butylamine gives a $n-\sigma$ complex involving the NH_2 group, and a $\pi-\sigma$ complex involving the CH_3 groups; $CHCl_3$ gives $n-\sigma$ and $\pi-n$ complexes involving the C−H and C−Cl bonds respectively; n-propylacetylene forms complexes of the $n-\sigma$ type (involving the acetylenic C−H bond) and of the $\pi-\sigma$ type (involving the CH_2 and CH_3 groups), etc. (see Tables 3 and 4).

It is comparatively simple to distinguish these complexes: $n-\sigma$ interaction generally leads to strong paramagnetic shifts on the protons, whereas $\pi-\sigma$ and $\pi-n$ interactions make a large contribution to the paramagnetic shift on carbon nuclei and a small contribution to the paramagnetic shift on protons. Aromatic molecules and alkene groups add on to radicals chiefly to give complexes of the $n-\sigma$ type (involving C−H bonds); interactions of the $\pi-\pi$ type are practically never observed, and apparently involve repulsion.

These regular features of complex formation have been confirmed for phenoxide and verdazyl radicals[107]; the complexes of nitroxide and phenoxide radicals with phenols have been extensively studied[108].

Complex formation by radicals changes the hyperfine interaction constants and the values of the g-factor[106]; this aspect is of particular importance when nitroxide radicals are used as spin tracers and probes. A situation is often realised in which a radical in two states—free and bound in a complex—has different frequencies of rotation and in addition is transferred from one state to another with a definite frequency. This dynamic problem has been solved[109]; the theoretical EPR spectra for different frequencies of exchange and rotation have been published[110].

Complex formation is also revealed in the rotational dynamics of molecules: the rotation about different axes is retarded indifferent ways, depending on how the molecules are attached to one another. Thus complex formation alters primarily the anisotropy of rotation. The rotation of the $CDCl_3$ molecule about the C_3 axis in benzene solution remains unchanged relative to the rotation in pure chloroform, but the rate of the rotation about the perpendicular axes is decreased by a factor of four[59]. This agrees with a structure of the complex in which the C−H bond of chloroform is adjacent and perpendicular to the plane of the benzene ring. In addition, the frequencies of the rotation of the molecules of benzene and chloroform in the complex about the common axis C_3-C_6 coincide,

that is the complex rotates as a whole, and there is no internal rotation about the C_3-C_6 axis[59].

The attachment of Ag^+, Na^+, or Li^+ ions to the CD_3CN molecule does not influence $D_\parallel$ but decreases $D_\perp$, that is the ions are attached to the CN group along the C_3 axis[59].

In conclusion, mention may be made of the measurement, by picosecond spectroscopy[111], of the characteristic time in which a free electron in water creates an equilibrium solvation layer, dropping into a potential well. This time is 4 ps, and corresponds to the rotational orientation time of dipolar molecules.

VII. INFLUENCE OF MOLECULAR DYNAMICS ON THE KINETICS OF CHEMICAL REACTIONS

The rate constant of a diffusion-controlled reaction k is equal to the product $k_{diff}P$, where k_{diff} is the rate constant of the encounters of the reacting particles, and P the probability of reaction in the pair. The quantity k_{diff} is determined entirely by the dynamics of the translational motion, and is usually estimated from the Smolukhovskii relationship[28]: $k_{diff} = 4\pi(r_A + r_B)(D_A + D_B)$, where r and D are the radii and diffusion coefficients of the interacting particles A and B.

The quantity P is determined by the molecular dynamics of the pair and is calculated from Eqn.(23), which contains the parameters of the diffusion (p, m) and chemical (k, ϵ) dynamics. The relative proportion of the primary and secondary reactions in the pair [first and second terms in Eqn.(23)] depends on the values of the constants k and ϵ; for large k and ϵ, the proportion of the primary reaction (that is reaction at the moment of first contact of the particles) is large; for small k and ϵ, an appreciable contribution to the probability of the reaction is made by the secondary encounters of the partners in the pair. The value of P also determines the cage effect in radical reactions; the same considerations apply to the primary and secondary recombination of the radicals in the pair. The cage effect and diffusion kinetics will not be discussed here; these topics have been dealt with in a number of reviews and monographs (see for example Refs.112 and 113).

The parameter ϵ (that is the probability of reaction in a contact pair) depends on the competition of the rotational and translational mobilities of the particles. It is usually described effectively using the black spot model. It is assumed that the reacting particles are spheres with marked anisotropy of the reactivity; in other words, the reaction centre occupies only a small fraction (the "black spot") of the surface of the sphere. If contact between two such spheres is to be accompanied by reaction, it is necessary that their relative orientation lead to the coincidence of the two "black spots". This model has been examined in detail[114]; the probability of reaction depends on the ratio of the frequencies of rotation and translation and on the size of the "black spot".

The "black spot" model has been confirmed by recent data[115] The disappearance of t-butyl radicals in C_7-C_{16} hydrocarbons is a diffusion-controlled process with rate constant 10^8-10^9 litre $mole^{-1}$ s^{-1}; the ratio of the yields of the disproportionation and recombination products (f_d/f_c) decreases with increase in temperature and decrease in the viscosity of the solvent. This dependence is explained as follows. For t-butyl radicals, disproportionation takes place in the pair for many relative orientations; in other words, the set of states from which disproportionation takes place is large, that is the "black spot" is large for disproportionation and small for recombination (the ratio of their areas is ~20). Increase in temperature and decrease in viscosity lead to an increase in the frequency of the rotations and an increase in the probability of contact of the "black spots" responsible for recombination; the probability of recombination therefore increases more rapidly than the probability of disproportionation. The ratio f_d/f_c should therefore decrease until it is determined purely by the chemical reactivity ($k_d/k_c \simeq 3$).

This dependence of f_d/f_c on temperature and viscosity, predicted by the "black spot" model, agrees with the experimental results. For reactions controlled by activation, that is taking place under kinetic conditions, molecular dynamics does not play a significant role; it may be revealed only in exceptional cases (in very viscous solutions or in reactions involving macro-molecules). For solid-phase reactions, on the other hand, even under kinetic conditions, the chemical kinetics are controlled by the molecular dynamics[116]; this is the fundamental difference between solid-phase and liquid-phase reactions.

Complex formation and solvation influence the kinetics of reactions controlled by both activation and diffusion. For reactions controlled by activation, the difference in the reactivities of the free and solvated particles is significant; the relative contributions of each to the reaction are determined by the corresponding rate constants and the solvation equilibrium constant[117]. Extensive data on the influence of solvation on the kinetics of reactions have been published[118,119]. For reactions controlled by diffusion, complex formation and diffusion influence both k_{diff} (via the translational dynamics) and P (via the reactivity and dynamics of the pair).

Thus solvation decreases the magnitude of the rate constant for the recombination of t-butoxide and peroxide radicals[119]. The diffusion coefficients of hydrocarbon molecules RH are much greater than the diffusion coefficients of the corresponding alkyl radicals R; it is suggested that this is due to solvation of the radicals[120]. The situation is particularly complicated when the solvated particles do not react, and the lifetime of the solvates is comparable with the lifetime of the pair; it is then necessary, in calculating P, to take simultaneous account of the dynamics of the pair and the dynamics of solvation.

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The dynamics of elementary processes in a liquid is part of chemical dynamics. It determines the competition of the elementary processes in pairs of reacting particles, diffusion kinetics, the efficiency of initiation in thermal, photochemical, and radiation-chemical processes, the efficiency of the utilisation and transformation of energy in chemical reactions, etc. The completeness of its description is of course still far from that for gaseous reactions (for example reactions in molecular beams), but it is being developed rapidly. The greatest contribution to the further development of this field is expected from picosecond spectroscopy.

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Structure of the Electrical Double Layer in Non-aqueous Solvents

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Systematic quantitative studies of the structure of the electrical double layer in non-aqueous solvents published during the past 10 years are reviewed. Methods for studying quantitatively the adsorption of ions at the electrode-solution (non-aqueous) interface are described, and the main experimental results on the specific adsorption of ions from non-aqueous media are summarised and compared with theoretical adsorption isotherms. The factors which determine the energy of adsorption and its dependence on the nature of the solvent, on the charge on the electrode, and on the number of pre-adsorbed particles are discussed. Existing models of the ionic double layer are tested for their ability to describe the specific adsorption of ions from non-aqueous solutions. Theoretical models of the fixed part of the electrical double layer are considered (in the absence of specific adsorption of ions), and used to interpret differential capacity curves in various solvents. 105 references.

CONTENTS

I. Introduction 932
II. Methods of quantitative study of the electrode-non-aqueous solvent interface 933
III. Specific adsorption of ions at the metal-non-aqueous solvent interface 936
IV. Special features of the double-layer models for non-aqueous solutions 940
V. Shape of the differential capacity curves and distribution of solvent molecules in the fixed part of the layer in the absence of specific adsorption of ions 944
VI. Conclusions 945

I. INTRODUCTION

Important new developments, associated with the use of non-aqueous solvents, have occurred in the last few years in both experimental and theoretical electrochemistry. In applied electrochemistry the practical aim of this work is to develop new cells in which the electrolyte consists of a non-aqueous solution. The electro-synthesis of organic compounds can also be carried out conveniently in non-aqueous solvents, since both organic and inorganic compounds are readily soluble in many non-aqueous solvents. Non-aqueous solutions are used in new electrochemical information-processing devices. The technical application of various solvents invariably leads to corrosion problems, and special studies of the corrosion of metals in contact with non-aqueous solvents have been reported. This work in applied electrochemistry underlines the importance of theoretical advances in our understanding of the kinetics and mechanisms of electrochemical reactions in non-aqueous media. Studies of the structure and properties of the electrical double layer and of adsorption phenomena at the electrode-non-aqueous solvent interface are an essential part of this type of work.

The first studies of the structure of the electrical double layer in non-aqueous solutions, based on measurements of electrocapillarity, were reported by Gouy[1] and by Frumkin[2,3]. Gouy measured the surface tension maxima of mercury in a series of non-aqueous solvents, and Frumkin plotted the full electrocapillary curves of the mercury electrode in methanol and ethanol, in pyridine, and in acetone. From these results Frumkin calculated the average double layer capacity for a negatively charged electrode, and he concluded that the effective dielectric constant within the electrical double layer bears little relation to the dielectric constant in the bulk of the solution[2,3]. Renewed interest in non-aqueous solvents in the early 1950's resulted in a series of publications on the electrochemistry of non-aqueous solutions and in particular on the structure of the electrical double layer. However most of this work is qualitative or, at best, semi-quantitative.

The first stage in the collection of qualitative data on the structure of the electrical double layer at the electrode-non-aqueous solvent interface was essentially completed in 1970. The results were fully reviewed by Payne[4,5]. The main conclusions can be summarised as follows.

1. There is a qualitative analogy between the mercury-water and the mercury-non-aqueous solvent interface. This analogy is most evident in the relative position of the electrocapillary and the differential capacitance curves for solutions of a series of surface-active anions[2-5].

2. The Gouy-Chapman-Grahame theory[6] of the diffuse part of the double layer is also applicable to non-aqueous solutions of surface-inactive electrolytes. In dilute solutions of these electrolytes a minimum appears in the differential capacitance curve near the zero charge potential, and the capacitance at the minimum varies with electrolyte concentration as predicted by the theory of the diffuse part of the electrical double layer[6]. This was first demonstrated by Grahame for NaF solutions in methanol[7], and later confirmed for other solvents[4,5,8,9].

3. General thermodynamic relationships (including those derived from the basic electrocapillarity equation) are applicable to the structure of the electrode-non-aqueous solvent interface. In particular, comparison of experimental electrocapillary curves with those calculated by double integration of the differential capacitance curves confirms the validity of the expression

$$C = -\partial^2\sigma/\partial E^2, \qquad (1)$$

where C is the double-layer capacitance, σ is the interfacial tension, and E is the potential[8-11].

4. The double-layer capacitance can be correlated with the thickness of the electrical double layer, determined by the size and shape of the solvent molecules[4,5,12], but it cannot be correlated with the bulk dielectric constant of the solvent.

Since Payne's review deals mainly with the boundary between a mercury electrode and the solution we shall discuss the above conclusions by considering the bismuth electrode, on which extensive experimental data have been

obtained in recent years by Pal'm and his colleagues of the Tartu State University (reviewed in Refs. 13 and 14).

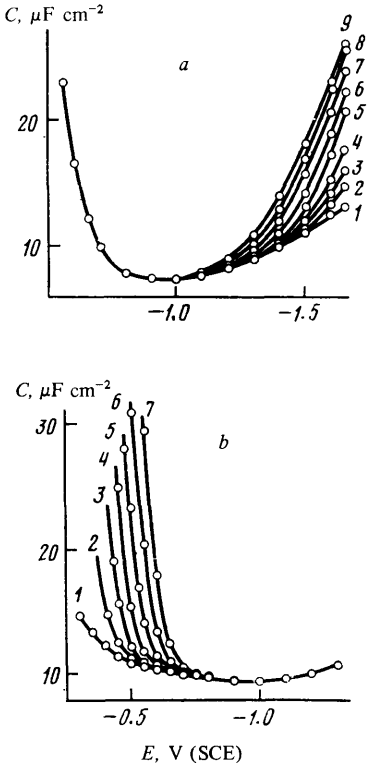


Figure 1. Differential capacitance curves for the Bi/C_2H_5OH interface in the following systems: (*a*) m*c* KSCN + $(1-m)c$ LiSCN for $c = 0.1M$ and the following values of m[*1*) 0, *2*) 0.005, *3*) 0.01, *4*) 0.02, *5*) 0.05, *6*) 0.1, *7*) 0.2, *8*) 0.5, *9*) 1.0]; (*b*) m*c* KCN + $(1-m)c$ KF for $c = 0.1M$ and the following values of m[*1*) 0, *2*) 0.003, *3*) 0.01, *4*) 0.03, *5*) 0.1, *6*) 0.3, *7*) 1.0] (from Ref. 14).

Fig. 1 shows the differential capacitance curves for the Bi/ethanol interface in mixtures of two salts at constant ionic strength[14]. The first of the two systems illustrates the replacement of the surface-inactive Li^+ cation by the surface-active K^+ cation, and the second illustrates the analogous replacement of the F^- by the CN^- anion. It can be seen from Fig. 1 that the capacity increases with the concentration of the surface-active component. A similar behaviour had been observed previously at a mercury electrode in aqueous solutions, for which the transition from an inactive to an active ion is accompanied by an increase in double-layer capacitance[15]. By using the reverse integration method[16] together with Eqn. (1) we can obtain two series of electrocapillary curves for the above systems to the precision of a single integration constant; in these curves an increase in the relative amount of surface-active ion is accompanied by a decrease in σ and a shift in the position of the electrocapillary maximum.

Fig. 2 shows the differential capacity curves of a bismuth electrode in ethanol solutions of the surface-inactive electrolyte $LiClO_4$.[17] In dilute solutions a characteristic minimum appears near the zero-charge potential (Fig. 2*a*). A plot of the reciprocal of the measured capacitance against the reciprocal of the calculated capacitance of the diffuse part of the double layer gives a straight line of unit slope, as expected from the theory of the electrical double layer (Fig. 2*b*).

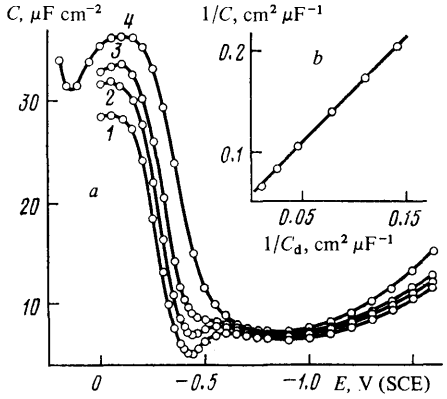


Figure 2. Differential capacitance of a bismuth electrode in standard solutions of $LiClO_4$: (*a*) capacitance against potential for various concentrations of $LiClO_4$ [*1*) 0.003, *2*) 0.01, *3*) 0.03, *4*) 0.5 *M*]; (*b*) reciprocal capacitance against reciprocal diffuse layer capacitance at zero surface charge (from Ref. 14).

The second stage in the study of the electrical double layer in non-aqueous solvents, with which the present review is mainly concerned, is characterised by quantitative studies of the adsorption of ions at the interface between the metal and the non-aqueous solvent. Quantitative data on the structure of the electrical double layer are needed to study the relationship between these results and the model structure of the double layer, to choose an isotherm which adequately describes the adsorption of ions, and to interpret the role of the non-aqueous solvent in determining the structure of the electrical double layer.

II. METHODS OF QUANTITATIVE STUDY OF THE ELECTRODE–NON-AQUEOUS SOLVENT INTERFACE

All the basic data on the structure of the electrical double layer at the boundary between *s,p* metals and aqueous solutions have been obtained by measurements of surface tension and differential capacity. However, the measurement of electrocapillary curves in non-aqueous solutions presents a number of difficulties. In experiments with the Gouy capillary electrometer[18,19] the non-aqueous solution often fails to wet the area between the mercury and the wall of the capillary (unlike aqueous solutions, which have a good wetting action). Thus the condition of full-wetting (which is essential in the capillary electrometer

method) is infringed, leading to unsatisfactory experimental results. In another method of measuring surface tension, based on squeezing a mercury drop from a U-shaped capillary[20], measurements in non-aqueous solutions are complicated by the need to achieve full wetting of the capillary tip whilst avoiding seepage of the solution into the capillary. In the case of aqueous solutions the combined requirements are met by making the capillary hydrophobic over its entire length before cutting off the capillary tip (which thus remains hydrophilic). In non-aqueous solvents this method is not applicable because the wetting powers of organic solvents towards hydrophobic and towards clean glass surfaces are almost identical. Thus, in spite of the large number of published studies of the double layer at the mercury/non-aqueous solution interface based on measurements of electrocapillary curves[8-11,21-27], the number of systems to which the method can legitimately be applied is limited by the above considerations. We should also note that the electrocapillary curve method cannot be used with solid electrodes. Therefore the most important method of studying the electrode/non-aqueous solution interface experimentally is the measurement of the differential capacitance of the electrical double layer.

Differential capacitance data can be used in two ways, which have been termed the binary electrolyte method[28-30] and the mixed electrolyte method[15,31]. In the case of a binary 1,1 electrolyte the surface excess of anions (Γ_-) for a given electrode charge q is calculated by the equation

$$\Gamma_- = (\Gamma_-)_{q=q^*} + (q - q^*)\left(\frac{\partial \Gamma_-}{\partial q}\right)_{q=q^*} - \frac{1}{2RT}\int_{q^*}^{q}\int_{q^*}^{q}\left[\frac{\partial (1/C)}{\partial \ln a_\pm}\right]_q dq^2, \qquad (2)$$

where q^* is the negative charge on the electrode (large enough to suppress the specific adsorption of anions), and $a_\pm$ is the mean activity of the electrolyte. The quantities $(\Gamma_-)_{q=q^*}$ and $(\partial\Gamma_-/\partial q)_{q=q^*}$ in Eqn. (2) are calculated by the formulae of the theory of the diffuse layer[29,30]. In order to use Eqn. (2) we must first of all determine the charge on the electrode by numerical integration of the C,E curves and plot $1/C$ against $\ln a_\pm$ for different (constant) values of q. The differentials $[\partial(1/C)/\partial \ln a_\pm]_q$ are then found by numerical or graphical differentiation of these curves.

The binary electrolyte method can be used if the following conditions are met. Firstly there must be a region of charge such that the charge of specifically adsorbed ions is $q_1^- = 0$. Secondly we must assume that the specific adsorption of counter-ions is negligible, and therefore that the charge q_1^+ of these ions in the fixed part of the double layer is zero. The condition $q_1^+ = 0$ must be met in the presence as well as in the absence of specific adsorption of anions. This is equivalent to assuming that the specifically adsorbed anions do not "drag" cations from the base electrolyte into the fixed part of the electrical double layer.

The second method relies on the use of a mixed electrolyte of constant ionic strength. To study the adsorption of the surface-active anion A* we use the system

$$mc\,\mathrm{KA^*} + (1-m)\cdot c\,\mathrm{KA}, \qquad (3)$$

where c is the total concentration of the solution, and m is the mole fraction of the surface-active anion A^* in the mixture with the inactive anion A. To study the adsorption of the surface-active cation K^* we use the system

$$mc\,\mathrm{K^*A} + (1-m)\cdot c\,\mathrm{KA}, \qquad (4)$$

where K is the surface-inactive cation. The characteristic C,E curves for systems (3) and (4) are shown in Fig. 1.

When the mixed electrolyte method is used to treat the experimental results there are two possible approaches. The first approach, used almost exclusively in the work reported so far, consists in the following. The q,E curves are first calculated by the reverse integration method, and then the change in the reciprocal of the differential capacitance $\Delta(1/C) = 1/C_0 - 1/C$ as between the inactive and the active electrolyte is calculated for a given charge on the electrode. The following equation is used:

$$q_1 = (zF/RT)\frac{\partial}{\partial \ln m}\int_{q^*}^{q}\int_{q^*}^{q}\Delta\left(\frac{1}{C}\right)\mathrm{d}\,q^2, \qquad (5)$$

where F is the Faraday and z is the charge on the ion. The second method of treating the experimental data in the mixed electrolyte method is proposed in Ref. 32, but it does not appear to have been used to date. It consists in plotting the reciprocal of the capacitance against the logarithm of the mole fraction in the mixture for q = const: these plots are then differentiated, and the differential is integrated twice with respect to charge:

$$q_1 = -(zF/RT)\int_{q^*}^{q}\int_{q^*}^{q}[\partial(1/C)/\partial \ln m]_q\,\mathrm{d}\,q^2. \qquad (6)$$

In principle Eqns. (5) and (6) should give the same value for the charge of specifically adsorbed ions (q_1).

The following assumptions are implicit in the mixed electrolyte method: 1) the surface-inactive reference ion can exist over the whole of the range of charges[31,33,34]; 2) the degrees of dissociation of the inactive and the active electrolyte are equal (note that substantial errors can arise if this assumption is not valid[35]); 3) the activity coefficients of the two electrolytes in the mixture are approximately equal[15,31] (the errors associated with the infringement of this condition, and ways of applying suitable corrections, are discussed in Refs. 36 and 37).

In order to describe the adsorption of ions we must not only determine the surface activity of various types of particle but also evaluate the adsorption characteristics of the double layer such as the ion–electrode interaction (the free energy of adsorption ΔG_A) and the ion–ion interaction in the adsorption layer (the repulsion interaction coefficient B). Hence the measured charge of specifically adsorbed ions is usually compared with the values calculated by using the adsorption isotherms. A detailed examination of experimental data and a theoretical discussion of the various types of isotherm[38-42] suggest that the most appropriate equation for the binary electrolyte is

$$\ln(q_1/zc) + zF\psi_0/RT = \ln\beta - 2Bq_1/z \qquad (7)$$

whereas the analogous isotherm

$$\ln(q_1/zmc) + zF\psi_0/RT = \ln\beta - 2Bq_1/z \qquad (8)$$

is the best for the mixed electrolyte. In these expressions the quantity $\ln\beta$, which is usually a linear function of the charge, i.e.

$$\ln\beta = a + bq, \qquad (9)$$

characterises the free energy of adsorption. The quantity ψ_0 is the potential of the outer Helmholtz plane, which can be calculated by the theory of the diffuse double layer. Thus for a 1,1 electrolyte we have

$$\psi_0 = (2RT/F)\,\mathrm{arcsinh}\left(\frac{q+q_1}{2Ac^{1/2}}\right), \qquad (10)$$

where $A = (\epsilon RT/2\pi)^{\frac{1}{2}}$ and ϵ is the dielectric constant of the solvent. The quantity B in Eqns. (7) and (8) is a measure of the repulsion interaction between the specifically adsorbed ions.

Eqns. (7) and (8) are a variant of the virial isotherm equation with the concentration of the ion in the bulk of the solution replaced by the concentration of the same ion in the outer Helmholtz plane. Thus the isotherm takes account of the so-called buffer action of the diffuse part of the electrical double layer, consisting in a contribution to the energy of an ion passing from the solution to the surface (since such an ion has to pass through the potential jump in the diffuse layer).

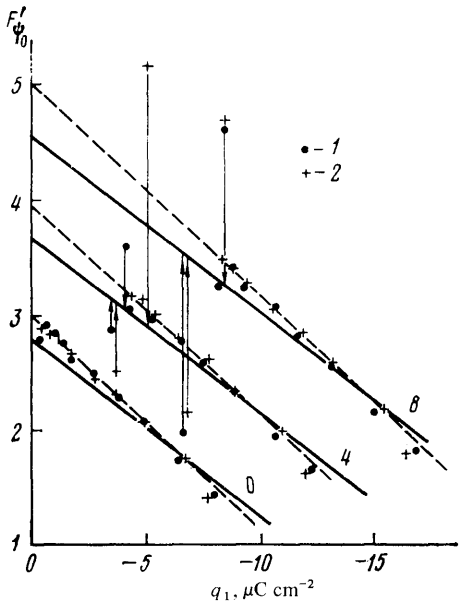


Figure 3. Plots of the quantity $F'_{\psi_0} = [\lg(q_1/zc) + zF\psi_0/2.3RT]$ against charge of specifically adsorbed anions for different electrode charges (stated against each curve in μC cm^{-2}). Full lines are theoretical plots obtained from Eqn. (7) with $a = 6.4$, $b = 0.51$, $B = 0.175$; the points and the broken curves are calculations by Eqn. (2) assuming the following uncertainties in the capacitance values: *1*) 0.1, *2*) 0.01 μF cm^{-2} (from Ref. 43).

The precision of the various methods has been assessed[32,43] by using Eqns. (7) and (8) under conditions of a charge of specifically adsorbed ions in excess of the charge on the electrode (in absolute value). As had already been pointed out[44,45], under the opposite conditions (i.e. $|q_1| < |q|$) the binary electrolyte method cannot be used to determine the specific adsorption of ions, and only the mixed electrolyte method offers reliable results. Hence it was interesting to compare the two methods under the condition $|q_1| > |q|$. This was done by assigning arbitrary values to the parameters a, b, and B, and using Eqns. (7) and (8) to calculate (on a computer) the variation of q_1, with q for various concentrations of the active component in the binary[43] or the mixed[32] electrolyte. The equation[43]

$$1/C = 1/C_{02} + (RT/FM)\left[2 - \frac{(2 - zbM)^2}{2 + M(z/q_1 + 2B)}\right] \qquad (11)$$

(where $M = [4A^2c + (q + q_1)^2]^{\frac{1}{2}}$ and C_{02} is the differential capacitance of the fixed layer at $q_1 = 0$) was then used to calculate the differential capacitance curves. The C values were rounded off to within 0.1 or 0.01 μF cm^{-2}, and the capacitance curves were then interpreted by the method described above[32,43]. This enabled the theoretical values of the parameters to be compared objectively with those obtained from the differential capacitance curves.

Table 1. Comparison of standard and calculated values of the parameters a, b, and B.

Parameter	Binary electrolyte method		Mixed electrolyte method	
	given	found	given	found
a	6.400	6.79	8.1500	8.24
b, cm^2 μC^{-1}	0.510	0.59	0.5900	0.61
B, cm^2 μC^{-1}	0.175	0.22	0.2125	0.23

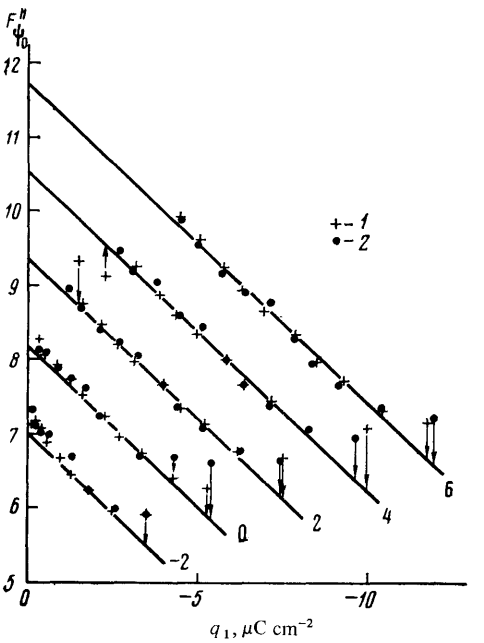


Figure 4. Plots of $F''_{\psi_0} = [\ln(q_1/zmc) + zF_{\psi_0}/RT]$ against charge of specifically adsorbed anions for different electrode charges (stated against each curve in μC cm^{-2}). Full lines are theoretical plots obtained from Eqn. (8) with $a = 8.15$, $b = 0.59$, $B = 0.2125$, and $c = 0.1$; the points were calculated by the mixed electrolyte method [*1*) by Eqn. (5), *2*) by Eqn. (6)] (from Ref. 32).

Fig. 3 shows plots of F'_{ψ_0} against q_1, where F'_{ψ_0} is the left-hand side of Eqn. (7), based on results obtained for a binary electrolyte[43]. The full lines are the initial plots,

corresponding to given values of the parameters a, b, and B, and the points were obtained from the C,E curves by the binary electrolyte method. Points *1* and *2* denote two different levels of precision in rounding off the differential capacitance values. We note a strong deviation of the "experimental" points from the ideal straight line, irrespective of the rounding off precision. Even the points which lie near the straight lines can be seen to fall on different straight lines, with a different slope and a different intercept. In other words, the binary electrolyte method can lead to serious errors in the determination of the parameters a, b, and B. We have shown[43] that the error of the binary electrolyte method can be minimised by increasing 1.5–2-fold the number of concentrations for which the differential capacitance curves are determined. Analogous data for a mixed electrolyte[32] are shown in Fig. 4. Though some of the points lie well away from the straight lines, most of the points lie exactly on the lines, and the experimental values of the parameters a, b, and B agree very well with the values assumed in the theoretical plots.

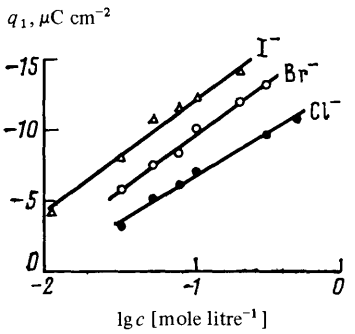


Figure 5. Specific adsorption isotherms of the Cl^-, Br^-, and I^- anions on a mercury electrode at a charge of +2 μC cm^{-2} from binary solutions in DMSO (from Ref. 30).

Our estimates of the precision of the binary electrolyte and the mixed electrolyte method are summarised in Table 1. We note that when $|q_1| > |q|$ the specific adsorption of ions is more accurately described by the mixed electrolyte method. Thus its use is recommended if the necessary conditions are met. In this respect the bismuth electrode has an important advantage, since it is easier to select a surface-inactive reference ion for the bismuth electrode than for the mercury electrode. This is due partly to the semiconductor properties of bismuth (which tend to lower the affinity of bismuth towards all anions) and partly to the fact that oxygen-containing solvent molecules are more strongly adsorbed on bismuth[13,14]. In the case of the mercury electrode there are systems for which no surface-inactive reference ion can be chosen[46]. Thus the results obtained on a bismuth electrode are currently the most appropriate for quantitative comparison of the specific adsorption of ions from non-aqueous solvents.

III. SPECIFIC ADSORPTION OF IONS AT THE METAL–NON-AQUEOUS SOLVENT INTERFACE

Let us examine first of all some experimental results. Fig. 5 shows the specific adsorption isotherms of the anions Cl^-, Br^-, and I^- at the interface between mercury and dimethylsulphoxide (DMSO) for $q = +2$ μC cm^{-2}. The isotherms have the characteristic semilogarithmic form, the surface activity of the anions increasing in the sequence $Cl^- < Br^- < I^-$ (i.e. as in aqueous solutions). Fig. 6 shows the specific adsorption isotherms of the Br^- anion for a range of solvents and an uncharged mercury surface.

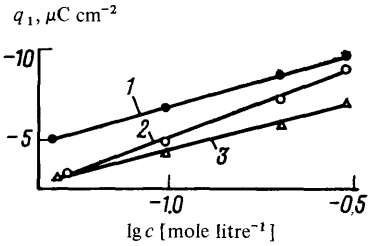


Figure 6. Specific adsorption isotherms of the Br^- anion on an uncharged mercury surface from binary solutions in different solvents: *1*) DMSO,[103] *2*) water[104], *3*) DMFA.[47]

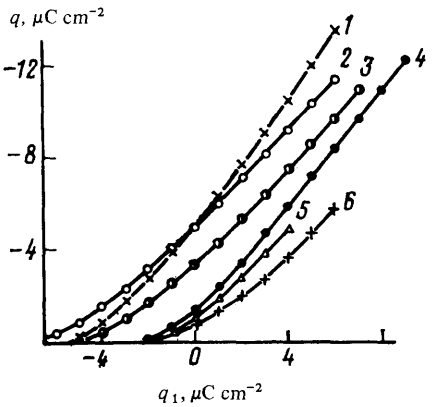


Figure 7. Charge of specifically adsorbed Br^- anions against charge of the Bi electrode (at $m = 0.1$) for the following solvents: *1*) AN, *2*) DMFA, *3*) DMSO, *4*) ethanol, *5*) methanol, *6*) water (from Ref. 14).

We note that the surface activity of Br^- increases from dimethylformamide (DMFA) to water and to DMSO, but the differences are not very large. Fig. 7 shows plots of q_1 against q for the adsorption of Br^- anions on Bi from six different solvents. We can see that for sufficiently high values of $q > 0$ the adsorbability of Br^- anions increases in the sequence water < methanol < ethanol < DMSO < DMFA < acetonitrile (AN).

In Figs. 8 and 9 we show some measurements of the specific adsorption of Cs^+ cations from various solvents on a negatively charged surface of bismuth or mercury. We note that the surface activity of the Cs^+ cations is greater at the mercury than at the bismuth interface for all solvents, i.e. that the nature of the metal has a marked effect. On the other hand the specific adsorption of Cs^+ on both metals (bearing a sufficiently negative surface charge) increases on going from water to DMFA, methanol, and ethanol. These results should be interpreted in conjunction with the changes in double-layer capacitance of sodium and caesium salts in various solvents. By comparing Figs. 9 and 10 we see that the increase in capacitance can be correlated qualitatively with the specific adsorption of caesium cations at the appropriate interface.

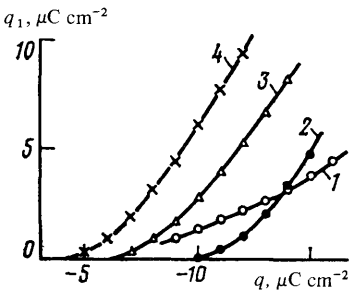


Figure 8. Charge of specifically adsorbed Cs^+ cations against charge of the Bi electrode (at $m = 0.1$) for the following solvents: *1*) water, *2*) DMFA, *3*) methanol, *4*) ethanol (from Ref. 14).

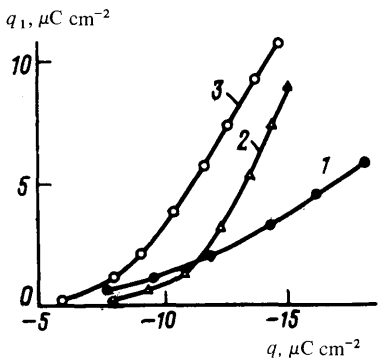


Figure 9. Charge of specifically adsorbed Cs^+ cations against charge of the Hg electrode (at $m = 1$) for the following solvents: *1*) water,[57] *2*) DMFA,[105] *3*) methanol[60].

It is interesting to consider the factors which determine the adsorption energy of the ions and the way in which this energy varies with the nature of the metal, that of the solvent, the charge on the electrode, and lastly the amount of adsorption already present on the electrode. A general solution of this problem must take account of the following interactions: metal and ion, metal and solvent, ion and solvent, adsorbed ions with themselves, and solvent molecules with themselves. We must also allow for the influence of the field due to the electrical double layer on all these interactions. Thus we can expect any general solution to be rather cumbersome.

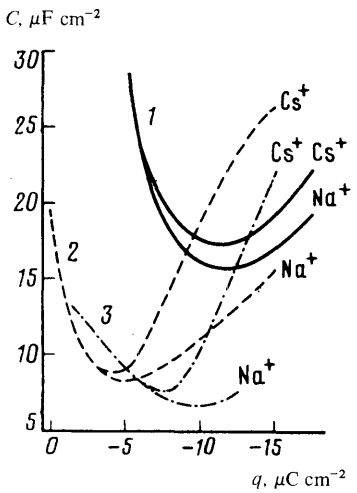


Figure 10. Cathodic portions of the plots of differential capacitance against electrode charge in 0.1 N solutions of sodium and caesium salts at the following interfaces: *1*) Hg/H_2O (chlorides)[57], *2*) Hg/CH_3OH (chlorides)[60], *3*) Hg/DMFA (perchlorates)[44].

Let us examine in detail the factors which influence the adsorbability of ions in different solvents. Since the specific adsorption of anions causes solvent molecules to be displaced from the surface, we can treat the adsorption process as a reaction in which solvent molecules are replaced by ions:

$$n\,S_{ads} + A_{bulk} \rightarrow A_{ads} + n\,S_{bulk}, \qquad (12)$$

where S denotes a solvent molecule, A is a specifically adsorbed ion (anion in this case), and n is the average number of solvent molecules displaced from the surface by one ion ($n \neq 1$). Evidently, the energy of adsorption of the ion from a given solvent ($\Delta G_{ads}^{(S)}$) will be greater, the stronger the interaction between the metal and the ion (ΔG_{M-A}), and it will be smaller, the stronger the interaction between the metal and the solvent (ΔG_{M-S}) as a result of the displacement of solvent molecules from the surface. It will also be smaller, the stronger the interaction between the ion and the solvent (ΔG_{A-S}), because the bonds between the ion and the solvent molecules are partially broken, and it will be greater, the stronger the interaction between the solvent molecules themselves (ΔG_{S-S}), because of the interaction between the displaced solvent molecules when they are transferred to the bulk of the solution. Thus the energy of adsorption of the ion A from the solvent S_1 can be written, according to Eqn. (12),

$$\Delta G_{ads}^{(S_1)} = \Delta G_{M-A} - n_1 \Delta G_{M-S_1} - \Delta G_{A-S_1} + n_1 \Delta G_{S_1-S_1}. \qquad (13a)$$

An analogous expression can be written for the solvent S_2 on the assumption that the quantity ΔG_{M-A} is independent of the solvent:

$$\Delta G_{ads}^{(S_2)} = \Delta G_{M-A} - n_2 \Delta G_{M-S_2} - \Delta G_{A-S_2} + n_2 \Delta G_{S_2-S_2}. \quad (13b)$$

We shall characterise the quantity ΔG_{M-S} by the work of adhesion referred to the limiting adsorption of solvent ($\Gamma_\infty^{(S)}$).[4,5] Using the Dupre equation we have

$$\Delta G_{M-S} = (\sigma_M + \sigma_S - {}_M\sigma_S)/\Gamma_\infty^{(S)}, \quad (14)$$

where σ_M is the surface tension (reversible surface work of the metal M), σ_S is the surface tension of the solvent S, and ${}_M\sigma_S$ is the interfacial tension (reversible surface work) of the M/S interface. If we equate[4,5] the quantity ΔG_{S-S} to one-half of the work of cohesion, also referred to $\Gamma_\infty^{(S)}$, we have

$$\Delta G_{S-S} = \sigma_S/\Gamma_\infty^{(S)}. \quad (15)$$

Subtracting (13b) from (13a), and using (14) and (15), we obtain

$$\Delta(\Delta G_{ads})^{(S_1-S_2)} = (\Delta G_{A-S_2} - \Delta G_{A-S_1}) + n_2(\sigma_M - {}_M\sigma_{S_2})/\Gamma_\infty^{(S_2)} - n_1(\sigma_M - {}_M\sigma_{S_1})/\Gamma_\infty^{(S_1)}. \quad (16)$$

But since $\Gamma_\infty^{(S_1)}/n_1 = \Gamma_\infty^{(S_2)}/n_2 = \Gamma_\infty^{(A)}$, where $\Gamma_\infty^{(A)}$ is the limiting adsorption of the anion A, Eqn. (16) simplifies to

$$\Delta(\Delta G_{ads})^{(S_1-S_2)} = (\Delta G_{A-S_2} - \Delta G_{A-S_1}) + ({}_M\sigma_{S_1} - {}_M\sigma_{S_2})/\Gamma_\infty^{(A)}. \quad (17)$$

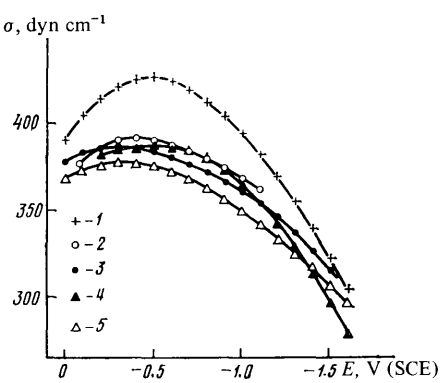


Figure 11. Electrocapillary curves of the mercury electrode for 0.1 *N* solutions of: *1*) Na_2SO_4 in water[18], *2*) NaCl in methanol[2], *3*) $NaClO_4$ in ethanol[2], *4*) KF in formamide[9], *5*) $NaClO_4$ in DMFA.[44]

Thus to the approximation of our present model the change in energy of adsorption of an ion on going from one solvent to another is determined by two factors: the difference in solvation energy and the different in surface tension of the metal in the two solvents, referred to the limiting loading of the surface by adsorbate. This conclusion had been arrived at earlier[47] for the transition from water to DMFA, but equality of the areas occupied by the ion and by the solvent molecule had been assumed (i.e. $n_1 = n_2 = 1$). The above argument does not rely on this assumption. Thus the use of Eqn. (17) to discuss the influence of the solvent on the adsorption energy of ions seems to be fully justified.

Let us consider first of all the effect of changes in interfacial tension. Fig. 11 shows the electrocapillary curves for a mercury electrode in solutions of various salts in water, methanol, ethanol, formamide, and DMFA. The σ, E curve for water (at low surface charges) lies significantly higher than the curves for the other solvents. Thus if we consider only the second factor we conclude that anions should be more readily adsorbed from aqueous than from non-aqueous solutions. However we see from Figs. 6 and 7 that this conclusion does not agree with experiment, and therefore the energy of solvation of the ions appears to play the predominant role.

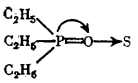
This result is not surprising if we remember that the change in energy of solvation of anions between water and various polar solvents is usually between 2 and 12 kcal mole^{-1}.[48] At the same time, putting $\Gamma_\infty^{(A)} \simeq 5 \times 10^{-10}$ mole cm^{-2} and noting from Fig. 11 that ${}_{Hg}\sigma_{H_2O} - {}_{Hg}\sigma_S \leq 40$ dyn cm^{-1}, we conclude that the ratio $({}_{Hg}\sigma_{H_2O} - {}_{Hg}\sigma_S)/\Gamma_\infty^{(A)}$ cannot be greater than 1.9 kcal mole^{-1}. On the other hand if we consider the adsorption of cations, which is most marked at high negative charges (when the surface tension is approximately the same in different solvents), we find that the second factor can be ignored to a first approximation. In this case the adsorption is determined only by the difference in solvation energy.

Let us examine the factors which determine the energy of solvation of ions and its change as between different solvents. The major part ($\geq 80\%$) of the energy of solvation accompanying the transfer of the ion from the gas phase into the solvent consists of the Born term, i.e. the energy gain due to purely electrostatic interactions between the charged particle and the medium (whose dielectric constant is substantially greater than unity[49]). However we are not concerned with the overall solvation energy, but with the difference in solvation energy as the ion is transferred from one solvent to another. The contribution of the Born term to this difference is quite small. Indeed, the well known Born formula for the solvation energy[50] gives the relative change in solvation energy on transferring the ion from a solvent of dielectric constant ϵ_1 to a solvent of dielectric constant ϵ_2 as $(1/\epsilon_2 - 1/\epsilon_1)$. .100%, i.e. less than 4% if the dielectric constants are greater than 25.

Thus the most important contribution to the change in solvation energy on transferring an ion from one polar solvent to another must come from factors other than the Born term. These could include, for example, hydrogen bond formation with anions in protonic solvents, whose effect should be most marked when the ion is transferred to an aprotic solvent (in which this factor is absent). Another relevant factor is the effect of the ion on the structure of the solvent, which may give rise to energy effects and thus contribute to the difference in solvation energy of the ion between two different solvents. Lastly we must allow for donor–acceptor interactions between the ion and the solvent molecule.

Up to recently it has been customary to characterise donor–acceptor interaction with allowance for hydrogen bond formation in terms of the donor number *DN*. According to Gutmann[48,51] the donor number is determined by the enthalpy of the reaction between a solvent molecule and $SbCl_5$ (i.e. of the reaction S + $SbCl_5$ = S.$SbCl_5$), in which the solvent S acts as a donor and $SbCl_5$ as an acceptor of electrons, thus: $DN \equiv -\Delta H_{S \rightarrow SbCl_5}$. However the experimental information most commonly available in studies of the specific adsorption of ions from non-aqueous solvents

concerns the adsorption of anions, which are themselves electron donors. Therefore the donor number is not a convenient way of comparing the adsorption of anions, and we prefer to use the acceptor number *AN*, recently proposed by Gutmann and coworkers[52,53]. The acceptor number can be determined by considering the interaction between solvent molecules and triethylphosphine oxide, which is an electron donor. As a result of donor–acceptor interactions of the type of



we observe a chemical shift of the ^{31}P signal in the NMR spectrum: it is suggested that the *AN* is proportional to $\delta^{31}P$. The acceptor number is normalised by the condition that the chemical shift $\delta^{31}P$ for the reaction $(C_2H_5)_3$. .PO + $SbCl_5$ corresponds to *AN* = 0 in hexane and *AN* = 100 in dichloroethane.

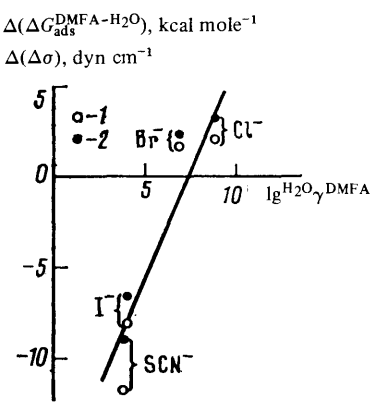


Figure 12. Change in surface activity of the anions Cl^-, Br^-, I^-, and SCN^- when transferred from water to DMFA against distribution coefficient of the ions between these two solvents. The surface activity of the anions on a mercury electrode is characterised by: *1*) the energy of adsorption at zero charge for $\Gamma_- \to 0$, *2*) the decrease in surface tension at the electrocapillarity maximum for $c = 0.1\ M$.

Gutmann has pointed out[52] that the acceptor number shows a good correlation with the energy of transfer of a chloride ion from acetonitrile to 12 different solvents. This observation confirms the validity of the acceptor number as an indicator of the change in solvation energy of a given ion on being transferred to different solvents. Of course, the donor–acceptor interaction is characterised by the properties of the ion as well as by those of the solvent (charge on the ion, and structure of the electronic shells[48,49]). Therefore the change in solvation energy of different ions being transferred from one solvent to another is not identical, and hence the corresponding change in the energy of adsorption of the ions is also not identical.

The change in solvation energy of ions of a given type being transferred from one solvent to another is conveniently characterised by the distribution coefficient of the ions between the two solvents. Fig. 12 shows a plot of the change in energy of adsorption of different ions on an uncharged mercury surface between water and DMFA against the logarithm of the distribution coefficient the ions between the same two solvents. These results suggest a good correlation between the change in solvation energy and the change in adsorption energy under the condition $M^{\sigma}S_1 - M^{\sigma}S_2 = \text{const}$. As Fig. 12 shows, the quantity $\Delta(\Delta G_{ads})^{(DMFA-H_2O)}$ on the vertical axis can be replaced by the change in the lowering of surface tension $\Delta(\Delta\sigma)$ produced by the ion at the maximum of the electrocapillary curve. If the vertical scale is properly chosen the plot against $lg\ S_{1\gamma}S_2$ is practically unchanged.

Unfortunately the distribution coefficients are not available for all the ions (and certainly not for all the solvents). Therefore we should look for a more general correlation between the energy of adsorption of the ion on the given electrode at $q = 0$ and the *AN* value of the solvent. If the potential of the outer Helmholtz plane (ψ_0) does not vary appreciably at $q = 0$ when the ion is transferred to a different solvent we can combine the term $zF\psi_0/RT$ in Eqns. (7) and (8) with the parameter $a_b = a + zF\psi_0/RT$, and use the latter parameter (a_b) to characterise the adsorption energy of the ion. Values of the parameter a_b for the adsorption of various ions on a bismuth electrode from various solvents are plotted in Fig. 13 against the acceptor number of the solvent. We note a good correlation between the change in adsorbability of the ion on bismuth and the acceptor number of the solvent, the difference in adsorbability between water and DMFA being greatest for the Cl^- anion and decreasing in the sequence

$$Cl^- > Br^- > I^- > SCN^-,$$

which reflects the effect of the nature of the ion. The small Cl^- anion is strongly solvated in aqueous solution as a result of hydrogen bond formation, whereas in aprotic solvents this ion is poorly solvated. As the size of the ion increases, so does its polarisability in dipolar aprotic solvents, thus compensating the solvation effects accompanying the transfer of the ion from water to DMFA. In the case of the large SCN^- anion the compensation is almost complete (see Fig. 13).

As expected, the adsorbability of anions increases as the acceptor number decreases. For the Cs^+ cations we note the opposite relationship (Fig. 13): the adsorption energy decreases on going from water to DMFA. Since a decrease in acceptor number should increase the solvation energy of cations, this result is not unexpected. However a comparison of the change in adsorbability of cations at zero charge with the results given above for high negative charges (Figs. 8–10) produces an apparent contradiction: the results for an uncharged surface are consistent with the change in acceptor number, whereas those for high negative surface charges are not. This discrepancy arises because the adsorption energy depends on the charge on the electrode as described in formula (9), where the parameter *b* is related to the structure of the electrical double layer.

Using the simple model of Grahame and Parsons[54,55] we obtain the following expression for the parameter *b* (see Ref. 38):

$$b = -zF/RTK_{12}, \qquad (18)$$

where K_{12} is the integral capacity of the space between the outer and the inner Helmholtz plane. Replacement of water by an organic solvent causes a relative displacement of the charged planes of the double layer, and K_{12} decreases whilst b increases. Therefore at high negative charges the adsorbability of cations in organic solvents can be greater than in H_2O, in spite of the smaller value of the a parameter. This effect is illustrated in Table 2 for the special case of the adsorption of Cs^+ cations at the Bi/H_2O and Bi/CH_3OH interfaces.

Table 2. Adsorption energy of Cs^+ and parameters of the double layer at the Bi/H_2O and Bi/CH_3OH interfaces for $q \leqslant 0$.

Interface	$a = (\ln \beta)_{q=0}$	K_{12}, $\mu F\ cm^{-2}$	b, $cm^2\ \mu C^{-1}$	$(\ln \beta)_{q=-15}$
Bi/H_2O	−1.4	93	−0.42	4.9
Bi/CH_3OH	−1.6	46	−0.85	11.2

Thus by allowing for the effect of the electric field on the adsorption energy of the ions we find that the changes in adsorption energy between different solvents are determined not only by the factors which appear in Eqn. (17) but also (and to a large extent) by a geometric factor: the relative size of the solvent molecules.

We should note that geometry considerations apply not only to the change in adsorption energy but also to the repulsion interaction between specifically adsorbed ions located in the inner Helmholtz plane. In practice the counter-ions reside in the outer Helmholtz plane, where they partially screen this repulsion effect, so that the screening effect is greatest (and the repulsion between the specifically adsorbed ions is weakest) when the inner and the outer Helmholtz plane are closest together. Since the molecules of non-aqueous solvents are larger than water molecules we expect the strongest repulsion effects in non-aqueous solvents[56]. As Fig. 14 shows, this expectation is borne out in a large number of systems[13,14]: the Figure is a plot of the virial coefficients B (which characterise the repulsion interaction in the adsorption of anions and cations on a Bi electrode from a number of solvents) against the quantity $(x_2-x_1)/x_2$, where x_1 and x_2 are the distance from the electrode surface to the inner and the outer Helmholtz plane respectively. Since the parameter B allows for the variation of the adsorption energy with the amount of pre-adsorbed particles this dependence of B on the ratio $(x_2-x_1)/x_2$ demonstrates one aspect of the influence of the nature of the solvent on the adsorption energy of ions.

Thus we have a fairly complex relationship between the specific adsorption energy of ions and the nature of the solvent, determined by the interaction of the solvent with the electrode surface, by ionic solvation effects, and by the geometry of the solvent molecules.

IV. SPECIAL FEATURES OF THE DOUBLE-LAYER MODELS FOR NON-AQUEOUS SOLUTIONS

As we have already pointed out, the isotherm which most rationally describes the adsorption of ions is one which allows for the buffer action of the diffuse double layer [see Eqns. (7) and (8)]. This can be illustrated by

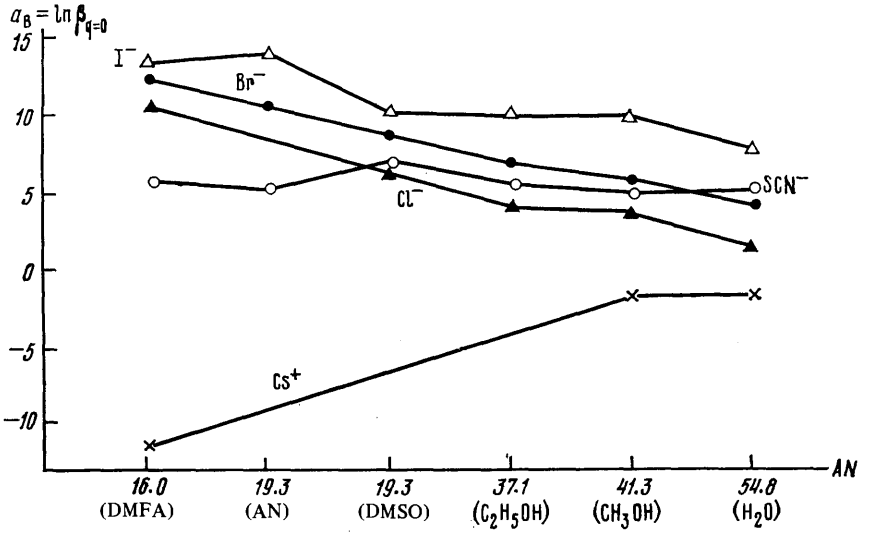


Figure 13. Adsorption of various ions on an uncharged bismuth surface against the acceptor number (AN) of the solvent. (a_b values taken from Ref. 14, AN values from Ref. 52).

considering the adsorption of caesium cations at the Hg/H_2O interface[38,57]. If we ignore the diffuse layer the adsorption isotherms in co-ordinates of $\ln(q_1/zmc)$ against q_1 give straight-line plots (Fig. 15). However these straight lines are not indistinguishable for systems with different ionic strength, and therefore the free energy of adsorption at $q_1 \to 0$ is a function of the concentration of the solution. This conclusion lacks physical significance, since there can be only one value of the energy of adsorption (which defines the system) for each value of the surface charge. However if we introduce a correction for the diffuse layer as in Eqn. (8) all the experimental points for systems with different ionic strength fall on a single straight line, and we obtain a unique value of the free energy of adsorption for each surface charge (Fig. 16). Similar results were obtained for the adsorption of K^+ and Rb^+ cations at the Bi/CH_3OH and Bi/C_2H_5OH interfaces[58].

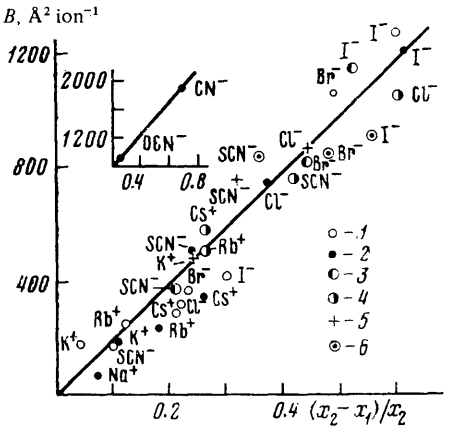


Figure 14. Plot of the second virial coefficient against the ratio $(x_2 - x_1)/x_2$ for the adsorption of various ions on the surface of a Bi electrode from the following solvents: *1*) water, *2*) methanol, *3*) AN, *4*) DMFA, *5*) ethanol, *6*) DMSO (from Ref. 14).

However complications arising from the incorporation of counter-ions into the fixed part of the double layer are often encountered in non-aqueous solvents. This process is favoured by the relatively smaller difference in dielectric constant (as compared with an aqueous medium) between the fixed and the diffuse part of the double layer, which allows ion pairs to be formed not only in the bulk but also within the fixed part of the double layer. The incorporation of counter-ions into the fixed part of the double layer can be illustrated by the adsorption of Cl^- on a bismuth electrode from ethanol[59]. The application of the isotherm equation (8) to the experimental results is shown in Fig. 17. We note that in the absence of a correction for the diffuse layer the plots of $\ln(q_1/zmc)$ against q_1 are rectilinear, but the straight lines for different concentrations do not coincide, and therefore different values of the adsorption energy are obtained for different concentrations at $q_1 \to 0$. On the other hand if the diffuse layer correction is applied, as in Fig. 17, the adsorption energy at $q_1 \to 0$ ceases to be a function of the ionic strength of the solution, though serious deviations from linearity are introduced.

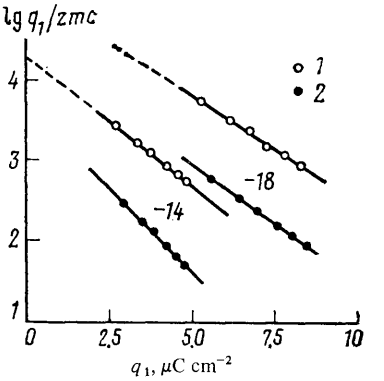


Figure 15. Plots of $\lg(q_1/zmc)$ against charge of specifically adsorbed Cs^+ cations in the system mc CsCl + $(1-m)c$ LiCl at the Hg/H_2O interface: *1*) $c = 0.01$ *M*, *2*) $c = 0.1$ *M*. The numbers against the curves denote the electrode charge in $\mu C\ cm^{-2}$ (from Ref. 57).

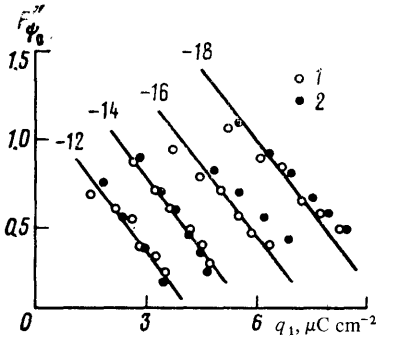


Figure 16. Plots of $[\lg(q_1/zmc) + zF\psi_0/2.3RT] = F\psi_0''$ against charge of specifically adsorbed Cs^+ cations for the system mc CsCl + $(1-m)c$ LiCl (from Ref. 38).

These deviations from linearity can be explained by postulating that counter-ions (in this case Li^+ cations) are attracted into the fixed layer by the specifically adsorbed Cl^- anions. In the calculation of the potential of the outer Helmholtz plane (ψ_0) which appears in Eqn. (8) we had assumed that $q_i^+ = 0$, i.e. that the Li^+ cations are not attracted into the fixed layer. This assumption appears to be unjustified. We shall now assume that the system is correctly described by Eqn. (8), and that the deviations from linearity are due to the incorporation of Li^+ cations into the fixed part of the double layer. We can therefore calculate the true potential of the outer Helmholtz plane from the magnitude of these deviations, and hence arrive

at the value of q_1^+. The number of cations (calculated in this way) is plotted in Fig. 18 against the number of specifically adsorbed anions. We can see that the points corresponding to different charges on the electrode all lie on the same curve, i.e. a definite relationship exists between the incorporation of cations and the specific adsorption of anions. This observation confirms the validity of our previous assumption, i.e. that the deviations from linearity of the plots of $[\ln(q_1/zmc) + zF\psi_0/RT]$ against q_1^- are due to the incorporation of counter-ions into the fixed part of the electrical double layer. This assumption stems directly from the concept of ion pair formation in the fixed layer, noting that the formation of ion pairs requires a definite stoichiometry of cations and anions.

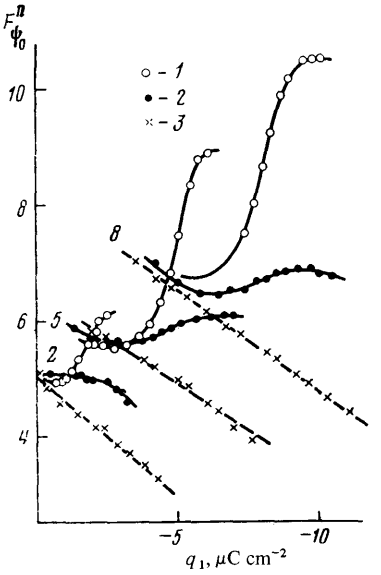


Figure 17. Plots of $[\ln(q_1/zmc) + zF\psi_0/RT] = F\psi_0''$ against charge of specifically adsorbed Cl^- anions in the system mc LiCl + $(1-m)c$ $LiClO_4$ at the Bi/C_2H_5OH interface: *1*) $c = 0.01$, *2*) $c = 0.1$, *3*) $c = 0.5$ *M*. The numbers against the curves denote the electrode charge in μC cm^{-2} (from Ref. 59).

The validity of our assumption can be demonstrated also by calculating the total surface excess of anions (Γ_-) in the double layer. The quantity Γ_- can be evaluated, in the first instance, by adding the charge of specifically adsorbed anions (q_1^-) and the charge due to the anions in the diffuse layer (q_2^-). The quantity q_2^- is calculated either by ignoring the incorporations of cations ($q_1^+ = 0$) or by allowing for the q_1^+ values (as shown in Fig. 18). Alternatively, the total surface excess Γ_- can be calculated by an independent method (the binary electrolyte method). By comparing the two methods we conclude[59] that the agreement between the plots of Γ_- against q is much better when allowance is made for the incorporation of cations in the fixed part of the double layer.

Similar irregularities in the plot of $F\psi_0'' = [\ln(q_1/zmc) + zF\psi_0/RT]$ against the charge due to specific adsorption can be observed in other systems, and in particular for the adsorption of Cs^+ cations at the Hg/CH_3OH interface[60].

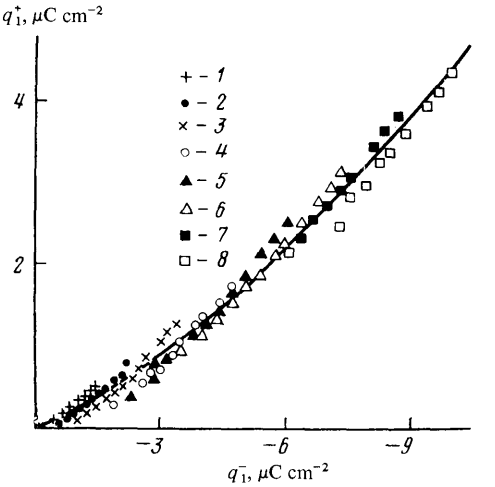


Figure 18. Charge of Li^+ cations incorporated into the fixed layer against charge of specifically adsorbed Cl^- anions in the system mc LiCl + $(1-m)c$ $LiClO_4$ at the Bi/C_2H_5OH interface for $c = 0.01$ *M*. The numbers denote the charge in μC cm^{-2} to which each type of point refers (from Ref. 59).

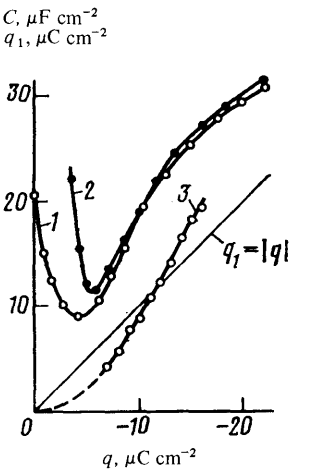


Figure 19. Differential capacity of a mercury electrode in 0.1 *N* methanolic solutions of (*1*) CsCl and (*2*) CsI, and charge of specifically adsorbed Cs^+ cations (*3*) in the same systems as a function of electrode charge.

As in the case of the adsorption of Cl^- ions at the Bi/C_2H_5OH interface, this system shows a surface overcharging effect, and therefore we may suggest that the deviations are due to the incorporation of anions into the fixed part of the

double layer. However the iodide anions attracted by the specifically adsorbed caesium cations could be expected to produce a greater increase in double-layer capacitance than the chloride anions. It is clear from Fig. 19 that this effect is not observed: at high negative charges the experimental C, E curves for 0.1 M methanolic solutions of CsCl and CsI are practically indistinguishable.

We can suggest two possible explanations: either the Cs^+ cations specifically adsorbed at the Hg/CH_3OH interface do not attract anions into the double layer (in which case we must look for another explanation of the deviation from linearity of the plot of $F\psi_0''$ against q_1), or the I^- and Cl^- anions have practically no effect on the capacity of the double layer when incorporated into the fixed layer. Anion adsorption (Cl^- or I^-) usually causes a sharp increase in capacitance when these anions are able to approach the surface, whereas the cations remain in the outer plane or are only partly attracted into the fixed layer. At high negative surface charges the caesium cations are apparently closer to the surface than the anions attracted into the fixed layer. If we ascribe the normal increase in capacity in the presence of iodide anions to partial charge transfer during adsorption[61,62], we cannot expect a large change in capacity to result from the incorporation of I^- anions into the fixed layer when the electrode is in the cathodic region and no charge transfer occurs during the adsorption of iodine. However the only rational criterion for choosing between the two alternative explanations is a direct programme of electrocapillary measurements. The problem remains unresolved at the moment.

The incorporation of counter-ions into the fixed part of the double layer cannot fail to complicate the model of the double layer, since the plane in which the counter-ions are located does not coincide (in general) with the plane of the specifically adsorbed ions. Hence we must consider two inner Helmholtz planes: one for the cations and one for the anions. These planes are situated at distances x_1^+ and x_1^- respectively from the electrode surface. This model of the electrical double layer is discussed in Refs. 63 and 64. Assuming additivity of the potential jumps associated with the charges q, q_1^+, and q_1^- we obtain the following expression[63,64] for the total potential jump in the fixed layer (ψ_u):

$$\psi_u = q/K_{02} + q_1^+/K_{1^+2} + q_1^-/K_{1^-2}, \qquad (19)$$

where K_{02} is the integral capacity of the whole of the fixed layer (from $x = 0$ to $x = x_2$), and K_{1^+2} and K_{1^-2} are the integral capacities of the regions between the outer Helmholtz plane ($x = x_2$) and the planes $x = x_1^+$ and $x = x_1^-$ respectively.

Assume that the specific adsorption consists of cations (for example, Cs^+ cations[64]), and that the charge q_1^- is due to incorporated counter-ions. Under these conditions $q_1^+ > |q_1^-|$ (for example, according to Palm and coworkers[64] $|q_1^-|/q_1^+ = 0.27$), and $x_1^+ < x_1^-$, so that

$$K_{1^-2} = \frac{\varepsilon}{4\pi(x_2 - x_1^-)} > K_{1^+2} = \frac{\varepsilon}{4\pi(x_2 - x_1^+)}.$$

Therefore Eqn. (19) can be re-written

$$\psi_u = \frac{q}{K_{02}} + \frac{q_1^+}{K_{1^+2}}(1 - \alpha_+), \qquad (20)$$

where the quantity $\alpha_+ = K_{1^+2}|q_1^-|/K_{1^-2}q_1^+$ is much smaller than unity. An analogous formula is obtained for the specific adsorption of anions:

$$\psi_u = \frac{q}{K_{02}} + \frac{q_1^-}{K_{1^-2}}(1 - \alpha_-), \qquad (21)$$

where the quantity $\alpha_- = K_{1^-2}q_1^+/K_{1^+2}|q_1^-|$ is also much smaller than unity, since under these conditions $q_1^+ < |q_1^-|$, and $K_{1^-2} < K_{1^+2}$.

Thus to a first approximation we can replace Eqn. (19) by the simpler expression of the Grahame–Parsons model[54]

$$\psi_u = q/K_{02} + q_1/K_{12}. \qquad (22)$$

For the specific adsorption of cations we now have $q_1 = q_2^+$ and $K_{12} = K_{1^+2}/(1-\alpha_+)$, and for the specific adsorption of anions $q_1 = q_1^-$ and $K_{12} = K_{1^-2}/(1-\alpha_-)$. It follows that K_{12} as defined in the Grahame–Parsons model[54] under conditions resulting in the incorporation of counter-ions in the fixed layer describes an effective capacity, slightly greater than the true capacity K_{1^+2} or K_{1^-2}. Therefore the simple Grahame–Parsons model can give a formal description of systems in which the specific adsorption of ions is accompanied by the incorporation of counter-ions into the fixed part of the double layer.

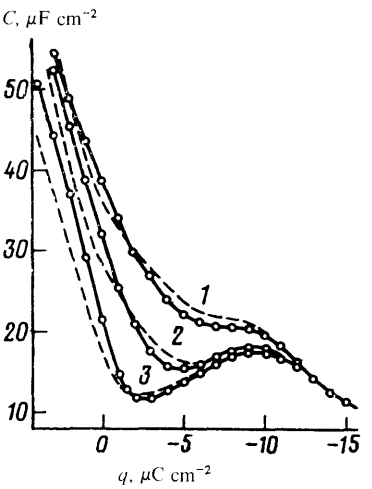


Figure 20. Differential capacity curves for a mercury electrode in *N*-methylformamide solutions of KBr of the following concentrations: *1*) 0.74, *2*) 0.1, *3*) 0.05 *M*. The full curves are experimental, the broken curves are calculated by Eqn. (11) for $a = 6.39$, $b = 0.72$ cm^2 μC^{-1}, and $B = 0.144$ cm^2 μC^{-1} (from Ref. 65).

As an example, we show in Fig. 20 a comparison of experimental C, q curves with the corresponding curves calculated by Eqn. (11) under conditions of specific adsorption of Br^- anions at the mercury/*N*-methylformamide (NMF) interface[65]. As we have already pointed out, Eqn. (11) was derived[43] from the Grahame–Parsons model. Hence the good agreement between experiment and calculation in Fig. 20 shows that the Grahame–Parsons model is formally applicable to the Hg/KBr in NMF system. On the other hand the incorporation of K^+ cations into the fixed part of the double layer through the specifically adsorbed Br^- anions cannot be excluded in this system. In other words, consistency between experimental results

and the Grahame–Parsons model cannot be taken as a general criterion for the absence of incorporated counter-ions in the fixed part of the double layer. A more detailed analysis is needed to establish the absence of counter-ions in the fixed layer[59].

V. SHAPE OF THE DIFFERENTIAL CAPACITY CURVES AND DISTRIBUTION OF SOLVENT MOLECULES IN THE FIXED PART OF THE LAYER IN THE ABSENCE OF SPECIFIC ADSORPTION OF IONS

The differential capacity curves of the fixed layer measured in different solvents can be arbitrarily classified into three groups[66]. The first group is characterised by a single maximum (or "hump"). C,q curves of this shape are obtained in water[67], formamide[9,68], and N-methylformamide[69], with a characteristic increase in capacity in the anodic region. To this group can also be assigned the C,E curves obtained in carbonates, lactones, and in sulpholane[26,70], in which the electrochemical process sets in before the anodic rise in capacity. The second group includes the C,E curves with a minimum, which do not show a "hump". Curves of this shape are typical of methanol[7], DMFA,[68] liquid ammonia[71], and some other solvents. Lastly we have the C,E curves with two "humps", observed in N-methylacetamide and N-methylpropionamide[4] (see curve *2* of Fig. 21).

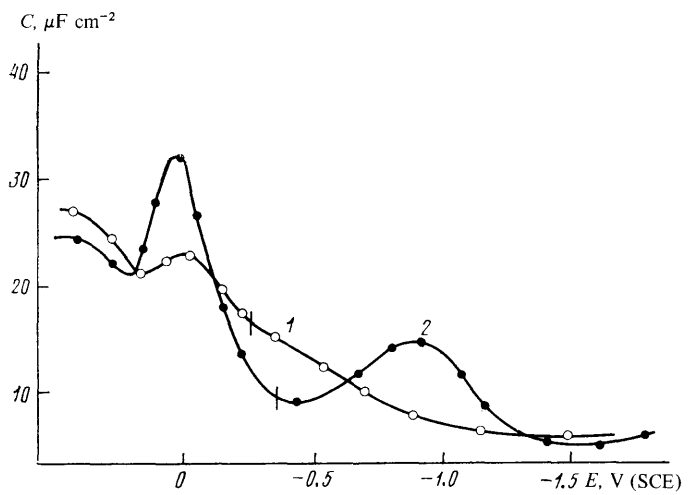


Figure 21. Differential capacity curves for a mercury electrode in 0.1 M solutions of KPF_6 in: *1*) dimethylacetamide, *2*) N-methylpropionamide. The vertical lines denote the position of the zero-charge potential (from Ref. 4).

The models of the fixed layer have been developed primarily for the interface between a metal and an aqueous solution. Thus, several workers[72–77] have discussed the presence of dipoles from the solvent on the electrode surface in two opposite orientations: with their negative pole or their positive pole pointing towards the surface. The relative number of dipoles in the two orientations depends on the charge on the electrode, and the "hump" on the C,q curve denotes equal numbers of dipoles in the two orientations.

Frumkin and coworkers[78,79] proposed a different model to explain the C,E curves of the gallium electrode. They assumed that solvent dipoles are chemisorbed with their negative pole pointing towards the surface: this would explain the experimentally observed increase in capacitance as the potential is made more positive.

Lastly, Damaskin and Frumkin[80] have described a model which combines the assumptions of the two previous models. They suggest that solvent particles can exist on the metal surface in two conditions: either as particles which can be freely oriented by the field of the double layer or as chemisorbed dipoles. Since the freely oriented particles and the chemisorbed dipoles cannot be identical, it is further suggested that the former consist of groups of several (usually three) associated molecules of water. The model was subsequently modified and improved[81–83]. In its most recent form the model describes in a quantitative way the dependence of the capacitance of the double layer on the electrode charge for the case of aqueous solutions of surface-inactive electrolytes on mercury, bismuth, and cadmium electrodes, and it correctly describes the temperature dependence of the capacity of the mercury electrode.

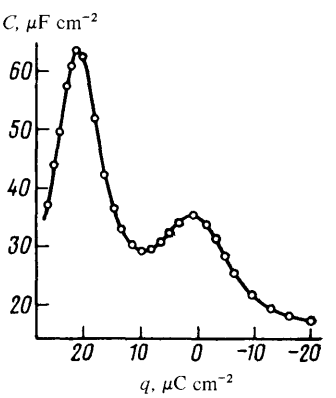


Figure 22. Differential capacity of the fixed part of the double layer against electrode charge according to a model which allows for the simultaneous presence of chemisorbed solvent dipoles and associated groups of dipoles able to orient themselves freely in the field of the double layer (from Ref. 83).

It is easy to show that this model (and none of the other models proposed so far) can account for all three types of differential capacitance curves in non-aqueous solvents[66]. Fig. 22 shows a C,q curve calculated by this model for a wide range of surface charge. If the region of the left-hand peak is not experimentally accessible as a result of electrochemical metal dissolution or solvent oxidation reactions this theoretical curve describes the variations in capacitance in the solvents of our first group. If the ideal polarisability region is even shorter, and only the middle part of the theoretical curve (between the two peaks) is experimentally accessible, the theoretical curve

describes the C,q curves of the second group of solvents. Lastly, for the general case the theory predicts a differential capacitance curve with two peaks as observed in *N*-methylacetamide and in *N*-methylpropionamide (see Fig. 22).

The following observations are also relevant. The position of the theoretical C,q curve along the horizontal axis is determined (if the associated groups of molecules can be freely oriented by the field) exclusively by the difference in energy level between a single solvent molecule forming part of the grouping and the same molecule present as a chemisorbed dipole. Under these conditions the right-hand maximum (or "hump") of the theoretical C,q curve is always found near $q = 0$. In order to shift the theoretical C,q curve towards more negative charges and thus align it with the experimental differential capacitance curves observed in amides we must make the further assumption that the associated groups have different stabilities in the two positions. The physical significance of this assumption is that the orientation of the associated groups depends both on the electric field of the double layer and on the structure of the solvent on the solution side. The structural orientation of the solvent dipoles determines the surface potential at the solution/air interface. The transition from the solution/air to the solution/metal interface causes a change in this surface potential, due both to the field of the double layer and to the specific interaction of the solvent molecules with the metal.

Thus the dipole component of the potential jump at the electrode/solution interface arises not only from the interaction of the solvent molecules with the electrode surface but also from the interaction of these molecules with similar molecules in the bulk of the solution. The work of Bagotskaya and Dubova[94] leads to the same conclusion: these workers compared the change in zero-charge potential of various metals and the change in adsorption-induced potential jump at the solution/air interface[85] for electrodes in water and in non-aqueous solvents respectively.

Studies of the adsorption of thiourea at the non-aqueous solvent/metal interface have helped to establish the structure of this interface. A great deal of information on the adsorption of thiourea on mercury and on bismuth from different solvents is now available[86–91]. However it is difficult to generalise these results because different models were used[86,89,91–93] in their theoretical analysis.

VI. CONCLUSIONS

This review shows that the quantitative study of the structure of the electrical double layer and of ionic adsorption at the metal/non-aqueous solvent interface has allowed us to reach some important conclusions as to the factors which determine the adsorption energy and the charge of specifically adsorbed ions, and also on some special features of the structure of this interface. Nevertheless workers in this field are still faced by many unsolved problems. The following are some of the most important problems currently being examined in the field of the structure of the electrical double layer and of adsorption phenomena at the interface between an electrode and a non-aqueous solution.

1. Further studies of mixed electrolyte systems in the region of $m \to 1$, where anomalous behaviour is sometimes reported (capacitance in a solution with $m = 1$ lower than in a solution with $m < 1$ for the same electrode charge[33,94]).

2. More extensive study of the effects arising from incorporation of counter-ions into the fixed part of the double layer; clarification of the role of the nature of the counter-ion and of the solvent[37,95]; influence of the adsorption of I^- anions (in the second layer) on the measured double layer capacity.

3. Development of a detailed model of the electrical double layer with two inner Helmholtz planes, to take account of the recent theoretical advances in this area[96,97].

4. Acquisition of additional experimental information on the adsorption of thiourea molecules at the metal–non-aqueous solvent interface, especially in dilute solutions (which sometimes show deviations from the classical theory of the diffuse layer[98]); generalisation of existing data on the adsorption of thiourea at various interfaces.

5. Detailed study of the structure of the fixed part of the double layer at the metal–non-aqueous solvent interface in the absence of specific adsorption of ions (measurement of capacity as a function of temperature, application of new relaxation methods with time constants of the order of nanoseconds, quantitative comparison of experimental data with model calculations).

6. Study of systems in which adsorption of ions is in competition with adsorption of solvent dipoles under conditions of strong specific interaction with the electrode surface, where interesting kinetic phenomena have been observed[99] but not fully investigated.

7. Study of systems with very strong chemisorption of solvent molecules on the electrode (for example, Pt or Ni). Only tentative results have so far been obtained[100–102] for systems of this type.

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Hydroxamic Acids and Their Metal Complexes

Y.K.Agrawal

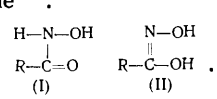
The chemical properties and thermodynamic characteristics of hydroxamic acids and their metal complexes are examined and Tables of proton-ligand and metal-ligand stability constants are presented. The influence of various factors on the dissociation of hydroxamic acids and their complexes is discussed.
The bibliography includes 123 references.

CONTENTS

I.	Introduction	948
II.	Proton-ligand stability constants or ionisation constants (pK_a)	948
III.	Thermodynamic functions for ionic equilibria	949
IV.	Proton-ligand stability constants in an aqueous medium	950
V.	Proton-ligand stability constants in mixed aqueous media	951
VI.	Metal-ligand stability constants	955
VII.	Determination of stability constants	956
VIII.	Linear free energy relations	957
IX.	The solvent effect	958
X.	Correlation between ionisation constants and the stability of the complex	958
XI.	The sequence of stability constants	959
XII.	Ionic charges and radii	960
XIII.	The ionisation potential and electronegativity	960
XIV.	The ligand field stabilisation energy	960

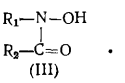
I. INTRODUCTION

Hydroxamic acids is the name given to *N*-acyl derivatives of hydroxylamine[1-3]:



(I) (II)

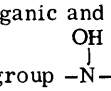
On the other hand, they can be regarded as *N*-hydroxy-derivatives of acid amides or as oximes of carboxylic acids[4]. The substitution of one or both hydrogen atoms in (I) or (II) by hydrocarbon or acyl groups yields compounds having the general formula



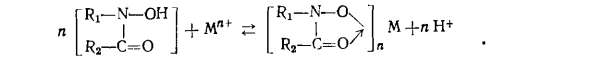
(III)

Here R_1 = H, phenyl, *o*-tolyl-, *m*-tolyl, *p*-tolyl, or *p*-chlorophenyl and R_2 consists of carboxylic or aliphatic acid derivatives.

Different terminologies are used for hydroxamic acids in the literature[1,3,5]. Thus in the publications of certain European workers a distinction is drawn between compounds designated above by odd and even numbers: the former are called "hydroxamic" acids and the latter are referred to as "hydroximic" acids. On the other hand, in certain American publications, including Chemical Abstracts[6-8], no such distinction is made and the general term "hydroxamic acids" is used for all compounds (I)-(III).

Hydroxamic acids are used in a wide variety of ways as reagents in organic and inorganic analysis. They contain the bidentate group  , which meets all the requirements necessary for the formation of metal complexes.

Complexes are usually formed via the substitution of a hydrogen atom of hydroxylamine by a metal cation and ring closure via the carbonyl oxygen atom:



The formation of metal chelates via this mechanism has for a long time constituted the basis of a wide variety of analytical methods[9-25]. Because of the non-ionic nature of such metal complexes (or inner complexes), they can be extracted in all cases from aqueous solutions or suspensions with the aid of solvents immiscible with water, such as benzene, chloroform, carbon tetrachloride, higher alcohols, or dichlorobenzene; separation processes involving solvent extraction are based on this feature. If such inner complexes are very sparingly soluble in water, are fairly stable, and have a constant composition, they can be used in gravimetric methods.

The study of the possible analytical applications of hydroxamic acids requires the knowledge of their ionisation constants[26,27]. In the search for reagents with improved analytical properties, numerous analogous compounds have been synthesised in recent years by introducing various substituents in different positions. For such specific synthesis to be successful, it is desirable to know the physicochemical properties of the reagents and their metal complexes; this would lead to a better understanding of the causes of the selectivity and sensitivity of the corresponding analytical reactions.

II. PROTON-LIGAND STABILITY CONSTANTS OR IONISATION CONSTANTS (pK_a)

The thermodynamic dissociation constants K_a(aq) of hydroxamic acids HA (dissociation via the reaction $HA \rightarrow H^+ + A^-$) in an aqueous medium are defined by the

formula

$$K_a(\text{aq}) = \frac{[H^+]\cdot[A^-]}{[HA]}\cdot\frac{Y_{H^+}\cdot Y_{A^-}}{Y_{HA}}, \quad (1)$$

or

$$p\,K_a(\text{aq}) = \lg[H^+] + \lg\frac{[HA]}{[A]} + 2\lg\frac{1}{Y_\pm}, \quad (2)$$

where $Y_\pm$ is the activity coefficient of a univalent ion ($Y_{H^+} + Y_{A^-} = Y_\pm$) at a given temperature and in a given medium; it is assumed that the activity coefficient of the unionised acid Y_{HA} is unity.

If the medium is altered by the addition of water, then, according to Van Uitert and Hass, the stoichiometric hydrogen ion concentration $[H^+]$ can be obtained from instrumental readings (B) with the aid of the equation

$$\lg[H^+] = B + \lg U_H^0 - \lg\frac{1}{Y_\pm}. \quad (3)$$

The values of $\lg U_H^0$ have been determined experimentally[28] and are listed in Table 1 for the dioxan–water medium.

Table 1. The values of $\lg U_H^0$ for water–dioxan media of different composition.

Dioxan concentration		$\lg U_H^0$ at 25°C		$\lg U_H^0$ at 30°C			$\lg U_H^0$ at 35°C
vol.%	mole fraction	this work	Ref.96	this work	Ref.97	Ref.96	this work
0	0	0.00	0.00	0.00	0.00	0.00	0.00
10	0.023	0.01	0.01	0.01	—	0.03	0.01
20	0.050	0.02	0.04	0.02	0.02	0.06	0.02
30	0.083	0.04	0.06	0.05	0.05	0.10	0.06
40	0.123	0.08	0.11	0.09	0.09	0.16	0.10
45	0.147	0.12	0.16	0.13	0.13	0.20	0.14
50	0.174	0.20	0.22	0.22	0.22	0.26	0.24
60	0.240	0.40	0.44	0.39	0.40	—	0.42
70	0.330	0.80	0.85	0.80	0.80	—	0.83

We have from Eqns. (2) and (3)

$$p\,K_a = B + \lg U_H^0 + \lg\frac{[HA]}{[A^-]} + \lg\frac{1}{Y_\pm}, \quad (4)$$

or

$$p\,K_a = B + \Delta, \text{ where } \Delta = \lg U_H^0 + \lg\frac{[HA]}{[A]} + \lg\frac{1}{Y_\pm}. \quad (5)$$

The values of Δ are listed in Tables 2 and 3.

III. THERMODYNAMIC FUNCTIONS FOR IONIC EQUILIBRIA

The standard free energy ΔF° of the ionisation reaction $HA \rightleftharpoons H^+ + H^-$ can be determined from the equation

$$\Delta F^0 = 2.303RT\ p K_a, \quad (6)$$

which can be written in a simplified form:

$$\Delta F^0(298.2°) = 1.365 p K_a \text{ (kcal)}; \quad (7)$$

$$\Delta F^0(308.2°) = 1.411\ p K_a \text{ (kcal)}. \quad (8)$$

The expression for the standard enthalpy of reaction ΔH° is obtained by integrating the van't Hoff equation for two temperatures T_1 and T_2:

$$\lg\frac{K_2}{K_1} = \frac{\Delta H^0(T_2 - T_1)}{4.576 T_1 T_2}. \quad (9)$$

Eqn. (9) is approximate, since ΔH° varies with temperature. However, for similar temperatures of the kind considered above (25° and 35°C), ΔH° can be assumed to be constant and Eqn. (9) can be written in the form

$$\Delta H^0 = 42.07 \Delta p K_a \text{ (kcal)}, \quad (9a)$$

where

$$\Delta p K_a = p K_a(25°) - p K_a(35°).$$

Table 2. The values of Δ at 25°C.

[HA]	[A⁻]	Dioxan concentration, vol.% (mole fraction)								
		0 (0)	10 (0.023)	20 (0.050)	30 (0.083)	40 (0.123)	45 (0.147)	50 (0.174)	60 (0.240)	70 (0.330)
0.009	0.001	0.97	0.98	0.99	1.02	1.07	1.10	1.19	1.43	1.87
0.008	0.002	0.62	0.63	0.65	0.68	0.73	0.77	0.87	1.13	1.61
0.007	0.003	0.39	0.41	0.42	0.46	0.51	0.56	0.67	0.93	1.43
0.006	0.004	0.02	0.22	0.24	0.28	0.33	0.38	0.48	0.75	1.27
0.005	0.005	0.03	0.05	0.07	0.11	0.16	0.22	0.32	0.51	1.11
0.004	0.006	−0.14	−0.12	−0.10	−0.06	−0.01	0.05	0.15	0.42	0.95
0.003	0.007	−0.33	−0.31	−0.29	−0.25	−0.19	−0.14	−0.03	0.24	0.78
0.002	0.008	−0.56	−0.54	−0.52	−0.48	−0.42	−0.37	−0.26	0.02	0.57
0.001	0.009	−0.91	−0.89	−0.87	−0.83	−0.77	−0.71	−0.68	−0.32	0.24

Note. 0.01 M acid is titrated with 0.1 M alkali introduced in ten equal portions, each portion corresponding to the neutralisation of one tenth of an equivalent of the acid.

Table 3. The values of Δ at 35°C.

[HA]	[A⁻]	Dioxan concentration, vol.% (mole fraction)								
		0 (0)	10 (0.023)	20 (0.050)	30 (0.083)	40 (0.123)	45 (0.147)	50 (0.174)	60 (0.240)	70 (0.330)
0.009	0.001	0.97	0.98	0.99	1.04	1.09	1.13	1.25	1.47	1.92
0.008	0.002	0.62	0.63	0.65	0.70	0.75	0.80	0.93	1.16	1.65
0.007	0.003	0.39	0.41	0.42	0.48	0.53	0.59	0.71	0.95	1.47
0.006	0.004	0.21	0.22	0.24	0.29	0.35	0.41	0.53	0.77	1.30
0.005	0.005	0.03	0.05	0.07	0.13	0.19	0.24	0.36	0.61	0.15
0.004	0.006	−0.14	−0.12	−0.10	−0.05	0.02	0.08	0—20	0.45	0.99
0.003	0.007	−0.33	−0.32	−0.29	−0.23	−0.17	−0.11	0—02	0.27	0.82
0.002	0.008	−0.56	−0.55	−0.52	−0.46	−0.40	−0.34	−0.21	0.05	0.61
0.001	0.009	0.91	−0.90	−0.87	−0.81	−0.74	−0.68	−0.55	−0.29	0.27

Note. 0.01 M acid is titrated with 0.1 M alkali added in ten equal portions; each portion corresponds to the neutralisation of one tenth of an equivalent of the acid.

The standard entropy of reaction $-\Delta S^\circ$ is usually calculated from the Gibbs–Helmholtz equation

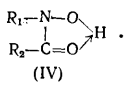
$$-\Delta S^0 = \frac{\Delta F^0 - \Delta H^0}{T}, \quad (10)$$

or

$$-\Delta S^0(25°) = 3.354 \cdot 10^{-3}(\Delta F^0 - \Delta H^0) \text{ (kcal)};$$
$$-\Delta S^0(35°) = 3.244 \cdot 10^{-3}(\Delta F^0 - \Delta H^0) \text{ (kcal)}.$$

IV. PROTON–LIGAND STABILITY CONSTANTS IN AN AQUEOUS MEDIUM

The ionisation constants of many substituted hydroxamic acids are listed in Table 4. These compounds are weak acids and, as has been observed for amides, the basicity of their nitrogen atom is also suppressed. In an aqueous medium and in dioxan–water mixtures the OH groups may be largely responsible for the acidity of hydroxamic acids. The suppression of the acid nature of these groups can then be accounted for by the intermolecular hydrogen bond formed by the compound. The formation of structure (IV) with intermolecular hydrogen bonds has been confirmed in several cases by infrared spectroscopy[30–33]:



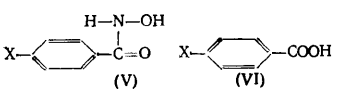
(IV)

Table 4. Proton–ligand thermodynamic stability constants (in an aqueous medium at 25 °C).

Hydroxamic acid	pK_a	Hydroxamic acid	pK_a
Benzo-	8.91	Aceto-	9.46
p-Methylbenzo-	9.05	n-Butyro	9.50
p-Methoxybenzo-	9.15	Propeno	9.52
p-Fluorobenzo-	8.81	Phenyloaceto-	9.23
p-Chlorobenzo-	8.70	Salicyl	7.43
p-Bromobenzo-	insoluble	α-Naphtho-	7.75
p-Iodobenzo-	insoluble	Picolino-	8.85
p-Nitrobenzo-	8.13	Nicotino-	8.27
p-Aminobenzo-	9.42	Isonicotino-	7.94
p-Cyanobenzo-	8.26	Chloroaceto-	8.52
N-Phenylbenzo-	8.38	*N*-Phenylnicotino-	8.12
N-Phenyl-*o*-methenobenzo-	8.49	Phthalo-	9.60
N-Phenyl-*o*-methylbenzo-	8.39	Indole-3-aceto-	9.70
N-Phenyl-*o*-chlorobenzo-	8.16	Cyclohexano-	9.87
N-*m*-Tolyl-*m*-nitrobenzo-	8.33	L-Lacto-	9.46
N-*p*-Tolyl-*m*-nitrobenzo-	insoluble	*p*-Chlorophenoxyaceto-	8.86
N-*o*-Tolyl-*m*-nitrobenzo-	8.15	Formo-	8.77
N-*p*-Chlorophenyl-*m*-nitrobenzo-*	insoluble	Glycine-	7.81
o-Hydroxybenzo-	9.05	D-Lysine-	8.05
o-Aminobenzo-	9.29	L-Lysine	8.04
Phenylaceto-	9.33		

*All the substituted *N*-*p*-chlorophenylbenzohydroxamic acids, obtained from *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-iodo-benzoic acids, are insoluble in water.

The thermodynamic ionisation constants of *p*-substituted benzohydroxamic acids listed in Table 5 are satisfactorily correlated with the Hammett constants:



(V) (VI)

X = H, CH_3, OCH_3, F, Cl, Br, I, NO_2, NH_2, or CN .

Table 5 shows that the pK_a values found experimentally and calculated from the Hammett equation and by the method of least squares agree satisfactorily, the maximum difference amounting to 0.03 pK_a unit.

Plots of the pK_a of hydroxamic acids (V) against the pK_a of benzoic acids (VI) and against the constants σ are presented in Figs. 1 and 2 respectively. The plots are linear and the following equation can be fitted by least squares:

$$pK_a = 1.02X + 4.62, \quad (11)$$

where X is the pK_a of the substituted benzoic acid. Similarly the plot of the pK_a of *p*-substituted benzohydroxamic acids (V) against the Hammett function σ is linear and has a slope of 1.00, which agrees satisfactorily with experimental values. The relation between acidity and the effect of the substituent introduced into the benzene ring is expressed by the constant ρ, whose values, derived from different plots (Figs. 1 and 2), are the same.

Table 5. Thermodynamic ionisation constants and Hammett constants for substituted benzohydroxamic acids.

No.	Benzohydroxamic acid		σ	pK_a (calc. by Eqn.(11))*	pK_a (calc. by Hammett Eqn.)	ΔpK_a**	pK_a for benzoic acid
	X	pK_a (expt.)					
1	H	8.91	—	8.91	—	±0.00	4.21
2	CH_3	9.05	−0.170	9.05	9.08	±0.00	4.34
3	OCH_3	9.15	−0.268	9.18	9.18	−0.03	4.47
4	F	8.81	+0.062	8.84	8.85	−0.03	4.14
5	Cl	8.70	+0.227	8.69	8.69	+0.01	3.99
6	Br	insoluble	+0.232	8.70	8.68	—	4.00
7	I	insoluble	+0.276	8.63	8.63	—	—
8	NO_2	8.13	+0.778	8.13	8.13	±0.00	3.44
9	NH_2	9.42	−0.660	—	—	—	—
10	CN	8.26	+0.660	8.24	8.25	0.02	3.55

*Obtained by the method of least squares as the average of nine values: $pK_a = 1.02X + 4.62$.
**ΔpK_a is the difference between the values of pK_a obtained experimentally and found from Eqn. (11).

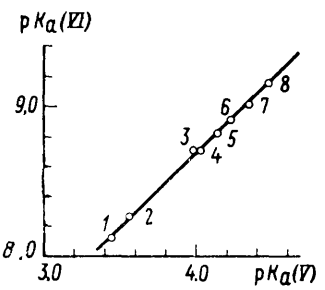


Figure 1. Relation between the pK_a values for benzoic acid (V) and benzohydroxamic acids (VI); substituent X: 1) NO_2; 2) CN; 3) Cl; 4) Br; 5) F; 6) H; 7) CH_3; 8) OCH_3.

The introduction of substituents into organic chelating compounds frequently alters their ability to form chelates and also influences other chemical and physical properties. Such changes in the acids have been studied on the basis of changes in their polarity, hydrogen bonding, and resonance and inductive effects.

In order to understand the relation between the molecular structure of hydroxamic acids and their pK_a values, it is necessary to investigate the pK_a of the initial carboxylic acids. All the hydroxamic acids (V) considered here were obtained from substituted benzoic acids (VI). Table 5 shows that the pK_a values for

hydroxamic acids form the same sequence as the pK_a for benzoic acids:

$$NH_2 > OCH_3 > CH_3 > F > Cl \simeq Br > NO_2 .$$

The introduction of the methyl group (X = CH_3), which has positive inductive and tautomeric effects, into (V) reduces the acidity. For the methoxy-group (X = OCH_3), which is an electronegative substituent[35], the positive tautomeric effect is much stronger than the inductive effect, which leads to a further decrease of acidity: $pK_a(OCH_3) > pK_a(CH_3)$. The strong influence of the nitro- and halogeno-substituents can be accounted for[36,37] by the mesomeric effect arising owing to the resonance between the benzenoid forms; in terms of this effect, halogens can be arranged in the sequence $F > Cl$; $Br > I$. Hydroxamic acids (Table 5) form the same sequence: compound 4 > compound 5; compound 6 > compound 7.

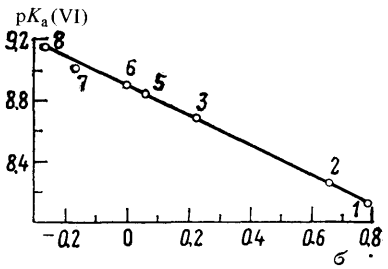


Figure 2. The Hammett relation for the pK_a values for benzohydroxamic acid; the significance of the circles is the same as in Fig. 1.

The nitro-group is a powerful *meta*-directing substituent with distinct electron-accepting properties, which increases the strength of benzoic acid, since pK_a(Hal) > $pK_a(NO_2)$; accordingly, the pK_a values for the compounds form the sequence 4–7 > 8 (Table 5).

V. PROTON–LIGAND STABILITY CONSTANTS IN MIXED AQUEOUS MEDIA

N-Arylhydroxamic acids are usually insoluble in water and readily dissolve in alcohol, dioxan, chloroform, etc. Their stability constants were therefore determined in dioxan–water mixtures of different compositions (10–70%) and were then extrapolated to the aqueous medium. The thermodynamic ionisation constants for certain hydroxamic acids are listed in Tables 6–8.

1. The Influence of Temperature

The ionisation constant of a weak acid is a function of temperature and usually has a maximum [K_a(max) or pK_a(min)] at approximately 25°C.[38] The data in Table 6 show that the pK_a for all hydroxamic acids in all solvents are lower at 35°C than at 25°C. The temperature corresponding to the maximum K_a can be found by determining pK_a at several temperatures, but it is evident that this temperature (T_{max}) must be higher than 25°C.

2. The Influence of the Medium

Agrawal and Tandon[39] observed that, with increase of the mole fraction of dioxan, the pK_a for hydroxamic acids also increases. This entails an intensification of the electrostatic interaction between the ions in a solvent with a low dielectric constant and facilitates the formation of molecular species. Gurney[40] and other workers[41,42] found that the change in standard free energy accompanying proton transfer ΔF°_{diss} can be represented by a sum of two components—electrostatic (ΔF°_{el}) and non-electrostatic (ΔF°_{nel}):

$$\Delta F^0_{diss} = \Delta F^0_{el} + \Delta F^0_{nel}, \qquad (12)$$

The electrostatic contribution to the free energy change can be estimated with the aid of the Born equation:

$$\Delta F^0_{el} = \frac{Ne^2}{2D}\left(\frac{1}{r^+} + \frac{1}{r^-}\right). \qquad (13)$$

For dilute solutions, D can be assumed equal to the dielectric constant of the solvent[43,44]; hence

$$pK_a = \frac{\Delta F^0_{nel}}{2.303RT} + \frac{Ne^2}{4.606RT}\left(\frac{1}{r^+} + \frac{1}{r^-}\right). \qquad (14)$$

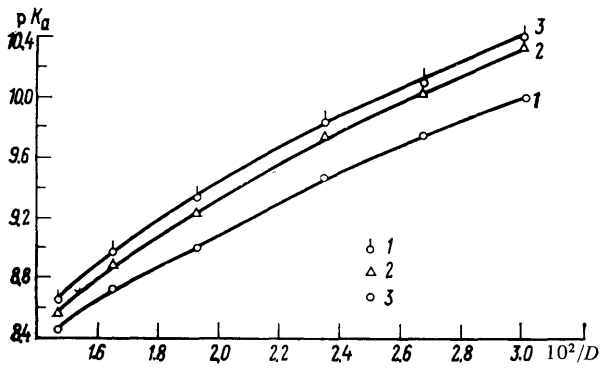


Figure 3. Dependence of pK_a on the dielectric constant (25°C): 1) *N*-*o*-tolylnitrobenzohydroxamic acid; 2) *N*-*m*-tolylnitrobenzohydroxamic acid; 3) *N*-*p*-tolylnitrobenzohydroxamic acid.

If it is assumed that ΔF°_{nel} is independent of the solvent, it is possible to plot pK_a against $1/D$. In certain cases, particularly for water-rich media, linear relations have been obtained[45–48], although deviations from linearity are not unusual either[49]. When such plots were constructed, it was observed that their curvature can vary. This is illustrated by typical curves in Fig. 3. Evidently non-electrostatic factors have a considerable influence on the dissociation of hydroxamic acids. Furthermore, a change in the dielectric constant and the consequent change in the shape and size of individual ions, hydrogen bonding, and other specific forms of solvent–solute interaction also have an appreciable influence on the dissociation of hydroxamic acids.

Table 6. Proton–ligand and metal–ligand stability constants for hydroxamic acids*.

Ion	NH_2OH	C_6H_4NHOH	o-CH_3–C_6H_4NHOH	m-CH_3–C_6H_4NHOH	p-CH_3–C_6H_4NHOH
			Benzohydroxamic acid		
H^+	gl; 0.5; 20; Aq; k_1=8.88[102]	gl; 0.1; 30; Aq; k_1=8.15[25]	gl; *T*; 25; 20d; k_1=9.32[62]	gl; *T*; 25; 20d; k_1=9.38[61]	gl; *T*; 25; 20d; k_1=9.43[61]
H^+	gl; 1.0; 20; Aq; k_1=8.68[102]	pH; 0.2; 25; Aq; k_1=8.15[100]	gl; *T*; 35; 20d; k_1=9.20[61]	gl; *T*; 35; 20d; k_1=9.25[61]	gl; *T*; 35; 20d; k_1=9.26[61]
H^+	pH; 0.1; 30d; Aq; k_1=8.80[103]	pH; 0.005; 25; 30c; k_1=8.28[19]	gl; *T*; 35; 20d; k_1=9.79[61]	gl; *T*; 25; 30d; k_1=9.84[61]	gl; *T*; 25; 30d; k_1=9.85[61]
H^+	—; 0.1; 25; Aq; k_1=8.75[105]	sp; —; —; —; k_1=8.27[101]	gl; *T*; 35; 30d; k_1=9.65[61]	gl; *T*; 35; 30d; k_1=9.75[61]	gl; *T*; 35; 30d; k_1=9.78[61]
H^+	E; 0.1; 25; Aq; k_1=8.79[106]	pH; —; 25; 50d; k_1=10.45[111]	gl; *T*; 25; 40d; k_1=10.32[61]	gl; *T*; 25; 40d; k_1=10.38[61]	gl; *T*; 25; 40d; k_1=10.42[61]
H^+	—; —; —; Aq; k_1=8.07[107]	pH; 0.1; 25; Aq; k_1=8.14[99]	gl; *T*; 35; 40d; k_1=10.25[61]	gl; *T*; 35; 40d; k_1=10.34[61]	gl; *T*; 35; 40d; k_1=10.35[61]
H^+	pH; 1.0,25; Aq; k_1=8.97[108]	pH; 0.005; 25; 50d; k_1=11.04[110]	gl; *T*; 25; 50d; k_1=11.12[61]	gl; *T*; 25; 50d; k_1=11.12[61]	gl; *T*; 25; 50d; k_1=11.13[61]
H^+	gl; [illegible] Aq; k_1=8.80[19]	pH; 0.005; 35; 50d; k_1=10.96[110]	gl; *T*; 35; 50d; k_1=10.95[61]	gl; *T*; 35; 50d; k_1=11.07[61]	gl; *T*; 35; 50d; k_1=11.03[61]
H^+	gl; 0.005; 25; 30c; k_1=9.30[19]	pH; 0.1; 30; Aq; k_1=8.14[111]	—; 0.1; 30d; Aq; k_1=8.18[99]	—	—; 0.1; 30; Aq; k_1=8.27[99]
H^+	sp; —; —; —; k_1=8.78[101]	pH; —; —; 70a; k_1=1026[112]	—	—	—
H^+	gl; 0.1; —; 30; Aq; k_1=8.48[99]	gl; *T*; 25; 20d; k_1=9.23[61]	—	—	—
H^+	gl; *T*; 25; Aq; k_1=8.91[96]	gl; *T*; 35; 20d; k_1=9.13[61]	—	—	—
H^+	gl; *T*; 35; Aq; k_1=8.79[26]	gl; *T*; 25; 30d; k_1=9.76[61]	—	—	—
H^+	—; 0.1; 30; Aq; k_1=8.43[109]	gl; *T*; 35; 30d; k_1=9.63[61]	—	—	—
H^+	—	gl; *T*; 25; 40d; k_1=10.30[61]	—	—	—
H^+	—	gl; *T*; 35; 40d; k_1=10.20[61]	—	—	—
H^+		gl; *T*; 25; 50d; k_1=11.04[61]	—	—	—
H^+		gl; *T*; 35; 50d; k_1=10.96[61]	—	—	—
H^+		gl; *T*; 25; Aq; k_1=8.91[26]	—	—	—
H^+		gl; *T*; 25; Aq; k_1=8.79[26]	—	—	—
H^+		gl; *T*; 25; 10d; k_1	—	—	—
H^+		gl; *T*; 35; 10d; k_1	—	—	—
H^+		gl; *T*; 25; 45d; k_1	—	—	—
			m-Methylbenzohydroxamic acid		
Cu^{2+}	—	gl; *T*; 25; 45d; k_1=10.65[27]	—	—	—
Cu^{2+}	—	gl; *T*; 35; 45d; k_1=10.62[27]	—	—	—
Cu^{2+}	—	gl; *T*; 25; 50d; k_1=11.08[4]	—	—	—
Cu^{2+}	—	gl; *T*; 35; 50d; k_1=11.04[27]	—	—	—
Cu^{2+}	—	gl; *T*; 35; 50d; k_1=10.35[59]; k_2=8.68	—	—	—
Zn^{2+}	—	gl; *T*; 35; 50d; k_1=8.63[59]; k_2=6.65	—	—	—
Ni^{2+}	—	gl; *T*; 35; 50d; k_1=7.77[59]; k_2=5.68	—	—	—
Mn^{2+}	—	gl; *T*; 35; 50d; k_1=6.80[59]; k_2=5.67	—	—	—
			p-Methylbenzohydroxamic acid		
H^+	—	gl; *T*; 25; 20d; k_1=9.35[61]	gl; *T*; 25; 20d; ins[61]	gl; *T*; 25; 20d; ins[61]	gl; *T*; 25; 20d; ins[61]
H^+	—	gl; *T*; 35; 20d; k_1=9.27[61]	gl; *T*; 35; 20d; ins[61]	gl; *T*; 35; 20d; ins[61]	gl; *T*; 35; 20d; ins[61]
H^+	—	gl; *T*; 25; 30d; k_1=9.84[61]	gl; *T*; 25; 30d; k_1=10.22[61]	gl; *T*; 25; 30d; k_1=9.96[61]	gl; *T*; 25; 30d; k_1=10.05[61]
H^+	—	gl; *T*; 35; 30d; k_1=9.75[61]	gl; *T*; 35; 30d; k_1=9.99[61]	gl; *T*; 35; 30d; k_1=9.88[61]	gl; *T*; 35; 30d; k_1=9.91[61]
H^+	—	gl; *T*; 25; 20d; k_1=10.49[61]	gl; *T*; 25; 40d; k_1=10.64[61]	gl; *T*; 25; 40d; k_1=10.57[61]	gl; *T*; 25; 40d; k_1=10.59[61]
H^+	—	gl; *T*; 35; 30d; k_1=10.33[61]	gl; *T*; 35; 40d; k_1=10.53[61]	gl; *T*; 35; 40d; k_1=10.46[61]	gl; *T*; 35; 40d; k_1=10.38[61]
H^+	—	gl; *T*; 25; 20d; k_1=11.13[61]	gl; *T*; 25; 50d; k_1=11.23[61]	gl; *T*; 25; 50d; k_1=11.32[61]	gl; *T*; 25; 50d; k_1=11.26[61]
H^+	—	gl; *T*; 35; 30d; k_1=10.98[61]	gl; *T*; 35; 50d; k_1=11.09[61]	gl; *T*; 35; 50d; k_1=11.10[61]	gl; *T*; 35; 50d; k_1=10.97[61]
H^+	—	gl; *T*; 35; 45d; k_1	—	—	—
H^+	—	gl; *T*; 25; 60d; k_1	—	—	—
H^+	—	gl; *T*; 35; 60d; k_1	—	—	—
H^+	—	gl; *T*; 25; 70d; k_1	—	—	—
H^+	—	gl; *T*; 35; 70d; k_1	—	—	—
Cu^{2+}	gl; *T*; 35; 50d; k_1=9.95[50]; k_2=8.12	gl; *T*; 25; 50d; k_1=10.30[111]	gl; *T*; 25; 50d; k_1=10.51[110]	gl; *T*; 25; 50d; k_1=10.52[110]; k_2=8.86	gl; *T*; 25; 50d; k_1=10.66[110]; k_2=8.87
Cu^{2+}	—	gl; *T*; 25; 50d; k_1=10.36[110]; k_2=8.78	gl; *T*; 35; 50d; k_1=10.40[110]; k_2=8.58		
Cu^{2+}	—	gl; *T*; 35; 50d; k_1=10.29[110]; k_2=8.63		gl; *T*; 35; 50d; k_1=10.50[110]; k_2=8.76	gl; *T*; 35; 50d; k_1=10.52[110]; k_2=8.69
			o-Methoxybenzohydroxamic acid		
H^+	—	gl; *T*; 25; Aq; k_1=8.49[26]	—	—	—
H^+	—	gl; *T*; 35; Aq; k_1=8.48[26]	—	—	—
H^+	—	gl; *T*; 25; 10d; k_1=8.84[39]	—	—	—
H^+	—	gl; *T*; 35; 10d; k_1=8.74[39]	—	—	—
H^+	—	gl; *T*; 25; 20d; k_1=9.24[39]	—	—	—
H^+	—	gl; *T*; 35; 20d; k_1=9.21[39]	—	—	—
H^+	—	gl; *T*; 25; 30d; k_1=9.84[39]	—	—	—
H^+	—	gl; *T*; 35; 30d; k_1=9.70[39]	—	—	—
H^+	—	gl; *T*; 25; 40d; k_1=10.36[39]	—	—	—
H^+	—	gl; *T*; 35; 40d; k_1=10.27[39]	—	—	—
H^+	—	gl; *T*; 25; 45d; k_1=10.70[39]	—	—	—
H^+	—	gl; *T*; 35; 45d; k_1=10.66[39]	—	—	—

* The following notation is used in Table 6 (and also in Tables 7 and 8): a = acetone; Aq = aqueous medium; d = dioxan (20 denotes a 20% dioxan solution); dis = distribution method; e = methods of measurement differing from those enumerated below; gl = potentiometric method using a glass electrode; ins = insoluble; pH = potentiometric titration method; sp = spectrometric method; *T* = thermodynamic constant; $k_1 = \lg k_1$ = logarithm of stability constant; "–" data not presented in given study. The horizontal rows present the following data: method, ionic strength/thermodynamic constant, temperature, medium, stability constants, reference; for example: gl (method; *T* (thermodynamic constant); 25 (temperature); 20d (medium consisting of a 20% dioxan solution); k_1 = 10.49 (logarithm of stability constant); [61] (reference).

Table 7. Proton–ligand and metal–ligand stability constants for hydroxamic acids*.

Ion	NH_2OH	C_6H_5NHOH	o-CH_3 C_6H_4NHOH
		Benzohydroxamic acid	
Cu^{2+}		gl; T; 35; 50d; k_1 = = 10.29[110] k_2 = 8.63	—
Fe^{3+}	B; 0.1; 20;Aq; k_1=11.06; k_2 = 9.37; k_3 = 7.40	sp; —; —; —; k_1 = 5.28	—
Fe^{3+}	dis; —; 25; —; k_1 =12.18	—	—
Mn^{3+}	gl; T; 35; 50d; k_1 = = 5,97[58]; k_2 = 4.52	gl; T; 35; 50d; k_1 = = 5.90[111]; k_2 = 10.80	gl; T; 25; 50d; k_1 = = 6.39[110]; k_2 = 5.62
Ni^{3+}	gl; T; 35; 50d; k_1 = =7.18[58]; k_2 = 5.14	gl; T; 25; 50d; k_1 = = 7.01[111]; k_2 = 5.91	—
Ni^{2+}	—	gl; T; 25; 50d; k_1 = = 7.0[110]; k_2 = 5.91	—
Ni^{2+}	—	dis; 0.1; 25; —; k_1 = = 6.10[112]; k_2 = 5.05	—
Th^{4+}	pH; —; 25;—; k_1=9.60[144]; k_2 = 9.21; k_3 = 8.95	dis; 0.1; —; —; k_1 = = 10.40[113]; k_2 = 9.90; k_3 = 9.00; k_4 = 8.10	—
UO_2^{2+}	pH; 0.1; 25; —; k_1= =8.72[108]; B_2 = 16.77	pH; 0.1; 30; —; k_1 = = 8.77[115]; k_2 = 8.21; B_2 = 16.98	pH; 0.1; 30; —; k_1 = = 8.64[115]; gl; T; 35; 50d; k_1 = = 10.20[117]; k_2 = 8.91
	pH; 0.1; 30; —; k_1 = = 9.03[115]; k_2 = 8.91; B_2 = 17.94	gl; T; 35; 50d; k_1 = = 70,59[116]; k_2 = 7.98	—
UO_2^{2+}	—	gl; T; 35; 50d; k_1 = = 10.72[117]	—
U^{4+}	pH; —; 25; —; k_1 = = 9,89[114]; k_2 = 8.11; k_3 = 8.32; k_4 = 6.62	—	—
Zr^{4+}	dis; —; 25; —; k_1 = = 12.43[108]; B_2 = 24.08	—	—
La^{3+}	—	pH; 0.1; 25; —; k_1 = = 7.28[118]; k_2 = 5.76	—
Pr^{3+}	—	pH; 0.1; 25; —; k_1 = = 7.70[118]; k_2 = 6.20	—
Nd^{3+}	—	pH; 0.1; 25; —; k_1 = = 7.88[118]; k_2 = 6.30	—
Sm^{3+}	—	pH; 0.1; 25; —; k_1 = = 8.28[118]; k_2 = 6.35	—
Eu^{3+}	—	pH; 0.1; 25; —; k_1 = = 8.45[118]; k_2 = 6.42	—
Cd^{3+}	—	pH; 0.1; 25; —; k_1 = = 8.36[118]; k_2 = 6.32	—
Dy^{3+}	—	pH; 0.1; 25; —; k_1 = = 8.60[118]; k_2 = 6.70	—
Er^{3+}	—	pH; 0.1; 25; —; k_1 = = 8.75[118]; k_2 = 6.70	—
Yb^{3+}	—	pH; 0.1; 25; —; k_1 = = 9.17[118]; k_2 = 6.95	—
Y^{4+}	—	pH; 0.1; 25; —; k_1 = = 8.00[118]; k_2 = 6.32	—
Be^{2+}	—	gl; 0.1; 35; 50d; k_1 = = 8.65[119]; k_2 = 7.20	—
Cu^{2+}	—	gl; T; 35; 50d; k_1 = =10.45[120]; k_2 = 8.90	—
Zn^{2+}	—	gl; T; 35; 50d; k_1 = = 8.16[120]; k_2 = 6.70	—
Ni^{2+}	—	gl; T; 35; 50d; k_1 = = 7.52[120]; k_2 = 6.01	—
Mn^{2+}	—	gl; T; 35; 50d; k_1 = = 6.33[120]; k = 5.99	—
		o-Methylbenozhydroxamic acid	
H^+	—	gl; T; 25; 20d; k_1 = 9.12[61]	gl; T; 25; 20d; ins[61]
H^+	—	gl; T; 35; 20d; k_1 = 9.02[61]	gl; T; 55; 20d; ins[61]
H^+	—	gl; T; 25; 30d; k_1 = 9.61[61]	gl; T; 25; 30d; k_1 = 9.87[61]
H^+	—	gl; T; 35; 30d; k_1 = 9.48[61]	gl; T; 35; 30d; k_1 = 9.68[61]
H^+	—	gl; T; 25; 40d; k_1 = 10.18[61]	gl; T; 25; 40d; k_1 = 10.45[61]
H^+	—	gl; T; 35; 40d; k_1 = 10.04[61]	gl; T; 35; 40d; k_1 = 10.35[61]
H^+	—	gl; T; 35; 40d; k_1 = 10.04[61]	gl; T; 35; 40d; k_1 = 10.33[61]
H^+	—	pl; T; 25; 50d; k_1 = 10.90[61]	gl; T; 25; 50d; k_1 = 11.13[61]
H^+	—	gl; T; 35; 50d; k_1 = 10.71[61]	gl; T; 35; 50d; k_1 = 11.02[61]
H^+	—	gl; T; 25; Ad; k_1 = 8.39[26]	—
H^+	—	gl; T; 35; Aq; k_1 = 8.32[26]	—
		m-Methylbenzohydroxamic acid	
H^+	—	gl; T; 25; Aq; k_1 = 8.58[26]	gl; T; 25; 20d; k_1 = 9.61[61]
H^+	—	gl; T; 35; Aq; k_1 = 8.53[62]	gl; T; 35; 20d; k_1 = 9.34[61]
H^+	—	gl; T; 25; 10d; k_1 = 8.91[26]	gl; T; 25; 30d; k^1 = 9.99[61]
H^+	—	gl; T; 35; 10d; k_1 = 8.88[27]	gl; T; 35; 30d; k_1 = 9.83[61]
H^+	—	gl; T; 25; 20d; k_1 = 9.29[27]	gl; T; 25; 40d; k_1 = 10.56[61]
H^+	—	gl; T; 35; 20d; k_1 = 9.26[27]	gl; T; 35; 40d; k_1 = 10.49[61]
H^+	—	gl; T; 25; 30d; k_1 = 9.76[27]	gl; T; 25; 50d; k_1 = 11.22[61]
H^+	—	gl; T; 35; 30d; k_1 = 9.74[27]	gl; T; 35; 50d; k_1 = 11.18[61]
H^+	—	gl; T; 25; 40d; k_1 = 10.30[27]	—
H^+	—	gl; T; 35; 40d; k_1 = 10.23[27]	—

* For the significance of the notation, see footnote to Table 6.

Table 8. Proton–ligand and metal–ligand stability constants for hydroxamic acids*.

Ion	C_6H_5NHOH	Ion	C_6H_5NHOH
	o-Methoxybenzohydroxamic acid		o-Bromobenzohydroxamic acid
H^+	gl; T; 25; 50d; k_1 = 11.09[39]	H^+	gl; T; 25; 10d; k_1 = 8.45[39]
H^+	gl; T; 35; 50d; k_1 = 11.03[39]	H^+	gl; T; 35; 10d; k_1 = 8.34[39]
Cu^{2+}	gl; T; 35; 50d; k_1 = 10.35[71]; k_2 = 8.68	H^+	gl; T; 25; 20d; k_1 = 8.86[39]
Zn^{2+}	gl; T; 35; 50d; k_1 = 8.63[80]; k_2 = 6.65	H^+	gl; T; 35; 20d; k_1 = 8.76[39]
Co^{2+}	gl; T; 35; 50d; k_1 = 7.96[80]; k_2 = 6.60	H^+	gl; T; 25; 30d; k_1 = 9.36[39]
Ni^{2+}	gl; T; 35; 50d; k_1 = 7.77[80]; k_2 = 5.68	H^+	gl; T; 35; 30d; k_1 = 9.26[39]
Mn^{2+}	gl; T; 35; 50d; k_1 = 6.80[80]; k_2 = 6.67	H^+	gl; T; 25; 40d; k_1 = 9.96[39]
	m-Methoxybenzohydroxamic acid	H^+	gl; T; 35; 40d; k_1 = 9.84[39]
H^+	—	H^+	gl; T; 25; 45d; k_1 = 10.30[39]
UO_2^{2+}	gl; T; 35; 50d; k_1 = 10.59[116]; k_2 = 8.00	H^+	gl; T; 35; 45d; k_1 = 10.20[39]
	p-Methoxybenzohydroxamic acid	H^+	gl; T; 25; 50d; k_1 = 10.66[39]
H^+	—	H^+	gl; T; 35; 50d; k_1 = 10.58[39]
UO_2^{2+}	gl; 0.1; 35; k_1 = 8.68[111]; k_2 = 8.35	Cu^{2+}	gl; T; 35; 50d; k_1 = 9.90[60]; k_2 = 7.97
	o-Fluorobenzohydroxamic acid	Zn^{2+}	gl; T; 35; 50d; k_1 = 7.49[60]; k_2 = 5.87
H^+	gl; T; 35; Aq; k_1 = 8.10[26]		o-Iodobenzohydroxamic acid
H^+	gl; T; 25; 10d; k_1 = 8.51[39]	H^+	gl; T; 25; 10d; ins[39]
H^+	gl; T; 35; 10d; k_1 = 8.43[39]	H^+	gl; T; 35; 10d; ins[39]
H^+	gl; T; 25; 20d; k_1 = 8.92[39]	H^+	gl; T; 25; 20d; k_1 = 8.92[39]
H^+	gl; T; 35; 20d; k_1 = 8.83[39]	H^+	gl; T; 35; 20d; k_1 = 8.80[39]
H^+	gl; T; 25; 30d; k_1 = 9.42[39]	H^+	gl; T; 25; 30d; k_1 = 9.60[39]
H^+	gl; T; 35; 30d; k_1 = 9.32[39]	H^+	gl; T; 35; 30d; k_1 = 9.30[39]
H^+	gl; T; 25; 40d; k_1 = 10.00[39]	H^+	gl; T; 25; 40d; k_1 = 10.00[39]
H^+	gl; T; 35; 40d; k_1 = 9.82[39]	H^+	gl; T; 35; 40d; k_1 = 9.90[39]
H^+	gl; T; 25; 45d; k_1 = 10.34[39]	H^+	gl; T; 25; 45d; k_1 = 10.35[39]
H^+	gl; T; 35; 45d; k_1 = 10.26[39]	H^+	gl; T; 35; 45d; k_1 = 10.25[39]
H^+	gl; T; 35; 50d; k_1 = 10.74[39]	H^+	gl; T; 25; 50d; k_1 = 10.75[39]
H^+	gl; T; 35; 50d; k_1 = 10.67[39]	H^+	gl; T; 35; 50d; k_1 = 10.63[39]
Cu^{2+}	gl; T; 35; 50d; k_1 = 10.03[60]; k_2 = 8.06	Cu^{2+}	gl; T; 35; 50d; k_1 = 9.96[60]; k_2 = 8.12
Zn^{2+}	gl; T; 35; 50d; k_1 = 7.40[60]; k_2 = 5.69	Zn^{2+}	gl; T; 35; 50d; k_1 = 7.40[60]; k_2 = 6.64
Mn^{2+}	gl; T; 35; 50d; k_1 = 6.10[60]; k_2 = 4.68	Ni^{2+}	gl; T; 35; 50d; k_1 = 7.23[60]; k_2 = 5.30
Ni^{2+}	gl; T; 35; 50d; k_1 = 7.36[60]; k_2 = 5.54	Mn^{2+}	gl; T; 35; 50d; k_1 = 6.20[60]; k_2 = 4.68
	o-Chlorobenzohydroxamic acid		o-Nitrobenzohydroxamic acid
H^+	gl; T; 25; Aq; k_1 = 8.16[26]	H^+	gl; T; 25; 20d; k_1 = 8.87[39]
H^+	gl; T; 35; Aq; k_1 = 8.05[26]	H^+	gl; T; 35; 20d; k_1 = 8.78[39]
H^+	gl; T; 25; 10d; k_1 = 8.43[39]	H^+	gl; T; 25; 30d; k_1 = 9.39[39]
H^+	gl; T; 35; 10d; k_1 = 8.31[39]	H^+	gl; T; 35; 30d; k_1 = 9.29[39]
H^+	gl; T; 25; 20d; k_1 = 8.85[39]	H^+	gl; T; 25; 40d; k_1 = 10.01[39]
H^+	gl; T; 35; 20d; k_1 = 8.79[39]	H^+	gl; T; 35; 40d; k_1 = 9.95[39]
H^+	gl; T; 25; 30d; k_1 = 9.35[39]	H^+	gl; T; 25; 45d; k_1 = 10.37[39]
H^+	gl; T; 35; 30d; k_1 = 9.23[39]	H^+	gl; T; 35; 45d; k_1 = 10.29[39]
H^+	gl; T; 25; 40d; k_1 = 9.93[39]	H^+	gl; T; 25; 50d; k_1 = 10.80[39]
H^+	gl; T; 35; 40d; k_1 = 9.81[39]	H^+	gl; T; 35; 50d; k_1 = 10.69[39]
H^+	gl; T; 25; 45d; k_1 = 10.28[39]	Cu^{2+}	gl; T; 35; 50d; k_1 = 9.45[60]; k_2 = 7.49[60]
H^+	gl; T; 35; 45d; k_1 = 10.14[39]	Zn^{2+}	gl; T; 35; 50d; k_1 = 7.12[60]; k_2 = 5.44
H^+	gl; T; 25; 50d; k_1 = 10.67[39]	Ni^{2+}	gl; T; 35; 50d; k_1 = 7.07[60]; k_2 = 5.04
H^+	gl; T; 35; 50d; k_1 = 10.56[39]	Mn^{2+}	gl; T; 25; 50d; k_1 = 5.74[60]; k_2 = 4.38
Cu^{2+}	gl; T; 35; 50d; k_1 = 9.96[60]; k_2 = 8.04		3,5-Dinitrobenzohydroxamic acid
Zn^{2+}	gl; T; 35; 50d; k_1 = 7.52[60]; k_2 = 5.92	H^+	gl; T; 35; 50d; k_1 = 9.66[116]
Ni^{2+}	gl; T; 35; 50d; k_1 = 7.23[60]; k_2 = 5.45	UO_2^{2+}	gl; T; 35; 50s; k_1 = 9.75[116]; k_2 = 7.01
Mn^{2+}	gl; T; 35; 50d; k_1 = 6.04[60]; k_2 = 4.93		
	2-Furohydroxamic acid		*N*-Butyrohydroxamic acid
H^+	gl; T; 25; 50d; k_1 = 10.73[61]	H^+	gl; T; 25; 50d; k_1
UO_2^{2+}	gl; T; 25; 50d; k_1 = 9.73[61]; k_2 = 8.36	H^+	gl; T; 35; 50d; k_1
Cu^{2+}	gl; T; 25; 50d; k_1 = 8.95[61]; k_2 = 7.42	Cu^{2+}	gl; T; 25; 50d; k_1 = 10.64[121]; k_2 = 8.87
Zn^{2+}	gl; T; 25; 50d; k_1 = 6.63[61]; k_2 = 5.81	Cu^{2+}	gl; T; 35; 50d; k_1 = 10.75[122]; k_2 = 8.97
Ni^{2+}	gl; T; 25; 50d; k_1 = 5.99[61]; k_2 = 5.12	Zn^{2+}	gl; T; 25; 50d; k_1 = 7.85[123]; k_2 = 6.40
Mn^{2+}	gl; T; 25; 50d; k_1 = 5.13[61]; k_2 = 4.39	Zn^{2+}	gl; T; 35; 50d; k_1 = 7.79[125]; k_2 = 6.30
Co^{2+}	gl; T; 25; 50d; k_1 = 5.81[61]; k_2 = 4.86	Ni^{2+}	gl; T; 25; 50d; k_1 = 7.61[121]; k_2 = 5.69
		Ni^{2+}	gl; T; 35; 50d; k_1 = 7.46[122]; k_2 = 5.50
		Mn^{2+}	gl; T; 25; 50d; k_1 = 6 23[121]; k_2 = 4.53
		Mn^{2+}	gl; T; 35; 50d; k_1 = 6.22[122]; k_2 = 4.46
		UO_2^{2+}	gl; T; 35; 50d; k_1 = 11.26[122]; k^2 = 9.51
		UO_2^{2+}	gl; T; 35; 50d; k_1 = 10.84[116]; k_2 = 8.19

* For the significance of the notation, see footnote to Table 6.

3. The Mole Fraction of Dioxan

When the mole fraction of dioxan is altered, an appreciable change in the pK_a is observed for all hydroxamic acids. The difference between the pK_a in water ($n_2 = 0$) and in a 70% dioxan–water mixture ($n_2 = 0.33$) is more than 4 pK_a units. The plot of the pK_a for hydroxamic acids against dioxan concentration is linear (Fig. 4). The

experimental values of the pK_a for almost all hydroxamic acids deviate from linearity by not more than 0.05 of a pK_a unit (i.e. by approximately 0.5%).

It is of interest to determine the accuracy of the pK_a values obtained by extrapolation to zero dioxan concentration (i.e. for $n_2 = 0$). In the case of hydroxamic acids for which data can be obtained in an aqueous medium it is possible to compare the extrapolated and experimental values. Table 9 shows that the agreement between them is satisfactory.

It is noteworthy that the validity of the extrapolation depends greatly on the availability of pK_a data in the region of low dioxan concentrations. The insolubility of the hydroxamic acid in 10 and 20% dioxan can hinder the extrapolation.

Table 9. Ionisation constants of hydroxamic acids in an aqueous medium.

Hydroxamic acid	Values obtained by extrapolation		Values obtained experimentally[a]		$T_pK = mn_2 + C$ (at 25°C)				$T_pK = mn_2 + C$ (at 35°C)			
	25°	35°	25°	35°	graphical method		least squares method		graphical method		least squares method	
					m	C	m	C	m	C	m	C
Benzo-	8.92	8.80	8.91[b]	8.70	10.05	8.92	10.10	8.92	10.00	8.80	10.10	8.79
N-Phenylbenzo-	8.55	8.45	8.38[c]	8.44	14.50[f]	8.55	14.95	8.46	14.51[d]	8.45	14.95	8.36
N-Phenyl-*o*-methoxybenzo-	8.52	8.46	8.49	8.48	14.85	8.52	14.90	8.52	14.86	8.46	14.90	8.45
N-Phenyl-*o*-methylbenzo-	8.44	8.28	8.39[d]	8.32	14.05	8.44	14.09	8.44	14.60	8.28	14.60	8.28
N-Phenyl-*o*-fluorobenzo-	8.18	8.10	—	8.10	14.80	8.18	14.75	8.18	14.78	8.10	14.75	8.09
N-Phenyl-*o*-chlorobenzo-	8.14	8.03	8.16[e]	8.05	14.70	8.14	14.65	8.12	14.66	8.03	14.65	8.01
N-Phenyl-*o*-bromobenzo-	8.14	8.01	—	—	14.85	8.14	14.80	8.12	14.90	8.01	14.85	8.01
N-Phenyl-*o*-iodobenzo-	8.18	8.09	—	—	14.82	8.18	14.85	8.17	14.85	8.09	14.85	8.07
N-Phenyl-*o*-nitrobenzo-	8.08	8.04	—	—	15.35	8.08	15.35	8.11	15.35	8.04	15.35	8.03
N-Phenyl-*m*-methylbenzo-	8.59	8.56	—	8.53	14.53	8.59	14.20	8.58	13.92	8.56	14.20	8.54

[a] This work.

[b] Priyadarshi[19] quotes pK_c values of 8.75 in 0.1 M KCl and 8.80; the calculated values of T_pK are 8.85 and 8.84 respectively.

[c] Taken from Priyadarshi[19].

[d] Taken from Shukla and Tandon[61].

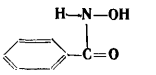
[e] According to the data of Dutta and Seshadari[99], pK_c = 8.08 at I = 0.1 M and 30°C; the calculated value is T_pK = 8.19.

[f] According to Dutta and Seshadari[99], pK_c = 7.60 at I = 0.1 M and 30°C; the calculated value is T_pK = 7.71.

4. Thermodynamic Functions

The pK_a values can be determined to within 0.02–0.03, whence the error of the determination of ΔF° is estimated as 0.03–0.04 kcal. The temperature coefficient method, normally employed for the calculation of ΔH°, can lead to a large error, because (1) the enthalpy of ionisation of acids is low and (2) the pK_a values have not been determined at many temperatures, which necessitates a more accurate graphical method for their estimation[50]. Eqn.(9a) shows that an error of 0.01 of a pK_a unit leads to an error in ΔH° of 0.42 kcal; the error in the determination of pK_a depends on the mutual cancelling or addition of errors in the pK_a values determined at two temperatures. Owing to the inherent deficiencies of the method, it is impossible to observe any definite tendencies in the variation of ΔH° as the medium is altered. This is illustrated by the data in Table 10 for benzohydroxamic acid (columns 4 and 5). It follows from the foregoing that ΔH° is best determined with the aid of the more accurate calorimetric method.

Table 10. The pK_a values for benzohydroxamic acid (BHA) calculated with the aid of thermodynamic functions*



Dioxan concn. vol.%	pK_a 25°	pK_a 35°	ΔpK_a	ΔH°
0	8.91	8.79	0.12	5.1
10	9.17	9.02	0.15	6.3
20	9.45	9.29	0.16	6.7
30	9.79	9.64	0.15	6.3
40	10.14	10.03	0.11	4.6
45	10.41	10.26	0.15	6.3
50	10.69	10.57	0.12	5.1
60	11.34	11.21	0.13	5.5
70	12.25	12.12	0.12	5.1

*Here $\Delta pK_a = pK_a(25^\circ) - pK_a(35^\circ)$; $pK_a(25^\circ) = 10.10n_2 + 8.92$; $r = 0.999$; $pK_a(35^\circ) = 10.10n_2 + 8.79$; $r = 0.999$ (r = correlation coefficient).

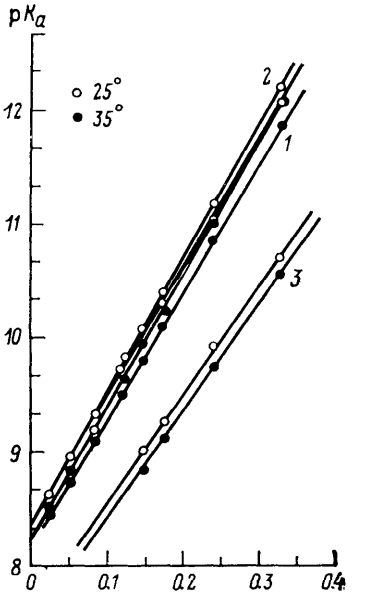


Figure 4. Dependence of pK_a on the mole fraction of dioxan: 1) *N*-phenylbenzohydroxamic acid; 2) *N*-*o*-tolyl-*m*-nitrobenzohydroxamic acid; 3) *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid.

Despite the relatively large errors in the values of ΔH° calculated by the temperature coefficient method, these data are very important, because they permit many important conclusions. At any rate, there is no doubt about the positive values of ΔH° found for all hydroxamic

acids in all solvents. This means that the ionisation reaction is endothermic below 25°C and becomes exothermic only above T_{max}. Furthermore, there is no doubt that the changes in ΔH° when the medium is altered are relatively small and are within the limits of experimental error. This is why the slopes of the linear plots of pK_a against n_2 are the same or almost the same at two temperatures for individual hydroxamic acids (Tables 6–8).

In the light of the foregoing, it would be correct to assume that ΔH° is to a first approximation independent of the medium, at least in the range of dioxan mole fractions 0–0.33.

Table 11. The free energies, enthalpies, and entropies of ionisation of hydroxamic acids*.

Thermodynamic functions	Dioxan concentration, vol.%						
	0	10	20	30	40	45	50
	X=OCH$_3$						
ΔF°	(11.62)	12.60	12.61	13.39	14.14	14.60	15.13
	(11.91)	12.38	12.99	13.68	14.48	15.03	15.55
(ΔH° 2.9) or $-\Delta S^\circ$	(29.1)	30.6	32.4	35.0	37.6	39.1	40.9
	(29.1)	30.6	32.6	34.9	37.4	39.2	40.9
	X=CH$_3$						
ΔF°	(11.52)	—	12.45	13.11	13.89	—	14.87
	(11.68)	12.10	12.78	13.32	14.27	14.67	15.26
(ΔH° 6.7) or $-\Delta S^\circ$	(16.1)	—	19.2	21.4	24.0	—	27.3
	(16.1)	17.4	19.6	21.4	24.5	25.7	27.7
	X=H						
	11.42	12 08	12.60	14.00	—	15.06	—
	11.69	12.32	12.87	13.58	14.38	—	15.67
(ΔH° 4.2) or $-\Delta S^\circ$	24.2	26.4	28.1	30.6	32.8	—	36.4
	24.3	26.3	28.1	30.4	33.0	—	36.5
	X=F						
ΔF°	(11.16)	11.61	12.17	12.85	13.65	14.12	14.65
	(11.40)	11.89	12.46	13.14	13.95	14.46	36.4
(ΔH° 2.8) or $-\Delta S^\circ$	(24.7)	26.2	28.1	30.4	33.1	34.6	36.4
	(24.7)	26.2	28.1	30.3	33.0	34.6	36.5
	X=Cl						
ΔF°	(11.08)	11.50	12.07	12.76	13.55	14.03	14.55
	(11.29)	11.72	12.39	13.01	13.83	14.30	14.89
(ΔH° 4.6) or $-\Delta S^\circ$	(21.6)	23.0	25.0	27.3	29.9	31.5	33.3
	(21.6)	23.0	25.2	27.2	29.9	31.4	33.3
	X=Br						
ΔF°	(11.08)	11.53	12.09	12.77	13 59	14.05	14.54
	(11.29)	11.75	12.35	15.05	13.88	14.38	14.92
(ΔH° 4.6) or $-\Delta S^\circ$	(21.6)	23.1	25.0	27.3	30.0	31.6	33.2
	(21.6)	23.1	25.0	27.3	30.0	31.6	33.4
	X=I						
ΔF°	(11.34)	insoluble	12.17	12.84	13.64	14.12	14.67
	(11.38)	insoluble	12.41	13.11	13.96	14.45	14.98
(ΔH° 4.2) or $-\Delta S^\circ$	(23.2)	insoluble	26.7	28.9	31.6	33.2	35.0
	(23.3)	insoluble	26.6	28.9	31.6	33.2	34.9
	X=NO$_2$						
ΔF°	(11.06)	insoluble	12.10	12.81	13.66	14.15	14.73
	(11.32)	insoluble	12.38	13.10	14.03	14.51	15.07
(ΔH° 3.4) or $-\Delta S^\circ$	(25.8)	insoluble	29.3	31.6	34.5	36.2	38.1
	(25.8)	insoluble	29.2	31.6	34.6	36.1	38.0
	Benzohydroxamic acid						
ΔF°	(12.15)	12.61	12.89	13.36	13.83	14.20	14.58
	12.40	12.72	13.10	13.59	14.14	14.46	14.90
(ΔH° 5.5) or $-\Delta S^\circ$	22.4	23.6	24.9	26.5	28.0	29.3	30.6
	22.5	23.5	24.8	26.3	28.1	29.2	30.5

*Here ΔF° and ΔH° are expressed in kcal mole^{-1} and ΔS° is expressed in cal mole^{-1} K^{-1}; the first value refers to 25°C and the second to 35°C. The values given in brackets have been obtained by extrapolation.

On this hypothesis, the values of ΔH° were calculated for different hydroxamic acids; they are equal to the difference between the intercepts made by the parallel lines on the pK_a axis multiplied by 42.07. The values of ΔH° calculated in this way are listed in Table 10, while the values calculated for each dioxan concentration have been deliberately omitted for reasons stated previously.

The errors in the determination of ΔF° and ΔH° are reflected in the values of ΔS°. Taking into account the considerations described in the preceding paragraphs, the values of ΔS° listed in Table 11 were calculated on the assumption that ΔH° is independent of solvent composition. It must be emphasised that ΔH° should change when the medium is altered. However, in the present study the influence of this factor was not observed and the simplifying assumption was made that ΔH° is independent of medium composition.

The usual tendency towards an increase of ΔS° with increasing content of dioxan in the solvent was noted. This tendency appears to be reliable and is observed also in the calculation of ΔS° from calorimetric values of ΔH°. If the acid ionises in two media—in water and in dioxan–water mixtures—the equations can be formulated as follows:

$$HA\,(aq) \rightleftarrows H^+\,(aq) + A^-\,(aq),$$
$$\Delta F^0\,(aq) = 2.303RT\,p K_a\,(aq). \qquad (15)$$

For mixed media, we have

$$HA \rightleftarrows H^+ + A^-,$$
$$\Delta F^0 = 2.303RT\,p K_a. \qquad (16)$$

Hence we have for the transfer reaction

$$HA + H^+\,(aq) + A^-\,(aq) \rightleftarrows HA\,(aq) + H^+ + A^-,$$
$$\Delta F^0 - \Delta F^0\,(aq) = 2.303RT\,(p K_a - p K_a\,(aq)) = 2.303RT\Delta p K_a. \qquad (17)$$

Thus, as shown above, the free energy ΔF° of the transfer reaction is proportional to the difference between the pK_a values in the aqueous and aqueous dioxan media. Hence it is readily seen that, since ΔH° is independent of the medium and is consquently zero for the transfer reaction, the changes in ΔF° are due to the changes in ΔS°. This can be illustrated in relation to benzohydroxamic acid for which ΔF°(aq) = 12.15 kcal mole^{-1} and $\Delta F^\circ(n_2 = 0.174)$ = 14.58 kcal mole^{-1}. Thus the transfer reaction entails a change in ΔF° by 2.43 kcal mole^{-1} due to the change in ΔS by 30.6 – 22.4 = –8.2 cal mole^{-1} K^{-1}.

VI. METAL–LIGAND STABILITY CONSTANTS

The stepwise formation of the hydroxamic acid complex (a 1 : 2 complex) can be represented as follows:

$$M^{n+} + HA \rightleftarrows MA^{(n-1)+} + H^+, \qquad (18)$$
$$MA^{(n-1)+} + HA \rightleftarrows MA_2^{(n-2)+} + H^+. \qquad (19)$$

The corresponding stability constants are defined in the following way:

$$k_1 = \frac{\{MA^{(n-1)+}\}}{\{M^{n+}\}\{A^-\}} = \frac{[MA^{(n-1)+}]}{[M^{n+}]\cdot[A^-]} \cdot \frac{Y_{MA}}{Y_{M+}\cdot Y_{A^-}} = k_1 \cdot \frac{Y_{MA}}{Y_M \cdot Y_A}; \qquad (20)$$

$$k_2 = \frac{\{MA_2^{(n-2)+}\}}{\{MA^{(n-1)+}\}\cdot\{A^-\}} = \frac{[MA_2^{(n-2)+}]}{[MA^{(n-1)+}][A^-]} \cdot \frac{Y_{MA_2}}{Y_{MA^+}Y_{A^-}} = k_2 \frac{Y_{MA_2}}{Y_{MA^+}Y_{A^-}}, \qquad (21)$$

where the symbols in curved brackets represent activities, Y are activity coefficients, and the symbols in square brackets are concentrations. The expressions for the constants K_1 and K_2 can be formulated thus:

$$\lg K_1 = \lg k_1 + 4\lg\frac{1}{Y_\pm}, \qquad (22)$$

$$\lg K_2 = \lg k_2 + 2\lg\frac{1}{Y_\pm}. \qquad (23)$$

where K_1 and K_2 are the thermodynamic stability constants and k_1 and k_2 are the molar contributions to the reversible reactions (18) and (19) respectively. Eqns. (22) and (23) can be obtained on the assumption that the activity coefficients of neutral species are unity and those of univalent negative and positive ions are approximately equal to the mean activity coefficient $Y_\pm$ of hydrochloric acid. In the limiting case where the Debye–Hückel law is applicable, we have $\lg Y_M^{2+} = 4 \lg Y_\pm$ (1 : 1).

In the study of equilibrium solutions it is customary to carry out measurements of concentration coefficients in media containing supporting salts at constant and high concentrations, which ensures a fixed ionic strength of the solution, so that the activity coefficients remain constant. Thus the concentration coefficients can be regarded as conventional constants applicable to solutions with the same supporting salt compositions as those used in the measurement of these constants.

There are three ways of obtaining experimental data for the calculation of thermodynamic constants: (1) experiments are performed in solutions which are sufficiently dilute for the concentrations to be set equal to the activities; (2) experiments are performed at different ionic strengths and the concentration coefficients are extrapolated to zero ionic strength; (3) corrections are applied for activity coefficients on the basis of the Debye–Hückel theory.

VII. DETERMINATION OF STABILITY CONSTANTS

Hydroxamic acids are weak acids and, when a complex is formed, there is competition between protons and metal ions for the ligand; the stability constant can be obtained by measuring the pH. pH measurements for the determination of stability constants are carried out by one or both methods presented below: (a) pH is measured as a function of ligand concentration; (b) pH is measured as a function of the amount of added acid (or base) at a constant metal ion and ligand concentration. In the second case the concentration of the free ligand, in excess relative to the amount required for complex formation, can be varied within wider limits than in the first case.

The stability constants can be calculated by the Bjerrum method[51] as developed by Calvin and Wilson[52]. The Bjerrum method has been examined theoretically by several workers[53–56].

The formation function $\bar{n}$, equal to the average number of coordinated groups per metal ion, is given by

$$\bar{n} = \frac{[MA] + 2[MA_2] + \ldots + N[MA_N]}{[M] + [MA] + [MA_2] + \ldots + [MA_N]} . \quad (24)$$

Using the expressions for the stability constant, it can be shown that $\bar{n}$ is a function of the free ligand concentration.

The values of $\bar{n}$ can be calculated in two ways. In the first procedure two titrations are carried out: initially, at a high concentration of added electrolyte the ligand is titrated with a standard solution of alkali, the pH change after each successive addition of alkali is noted, and the corresponding curve is plotted. One then titrates with alkali a mixture of the metal ions and the ligand in the presence of the same electrolyte and a plot is again constructed. The second titration curve lies significantly below the curve for the ligand alone; the decrease in pH shows that complex formation leads to neutralisation of the solution. The distance between the two titration curves in the horizontal direction yields the total number of ligand linkages and its division by the total concentration of metal ions makes it possible to obtain $\bar{n}$.

In the second case the free ligand concentration is calculated from the principle of electroneutrality. Substitution of this concentration in Eqn. (5) gives $\bar{n}$:

$$\bar{n} = \frac{A^0 - [A^-]}{M^0} , \quad (25)$$

where $[A^-] = 1 + [H^+]/k_1 + [H^+]^2/k_1k_2 + \ldots + [H^+]^n/k_1k_2 \ldots k_n$ and A^0 and M^0 are the total ligand and metal ion concentrations respectively.

The free ligand concentration can be determined as follows: the concentration of undissociated acid is equal to the difference between the total acid concentration ions and the concentration of acid which has reacted and dissociated:

$$[HA] = A^0 - C_{OH} - [H^+] - [OH^-]. \quad (26)$$

We have from Eqn. (1)

$$K_a = \frac{1}{q_H} \cdot Y_\pm^2,$$

where

$$q_H = [HA]/[H^+]\,[A^-]$$

or

$$\lg q_H = \mathrm{p}K_a - 2 \lg \frac{1}{Y_\pm} .$$

On substituting the expression for [HA] in Eqn. (26), we obtain

$$[A^-] = \frac{A^0 - C_{OH} - [H^+] - [OH^-]}{q_H [H^+]} . \quad (27)$$

The stability constants are calculated for different values of $\bar{n}$ and the corresponding values of $[A^-]$ by solving a system of N equations. Block and McIntyre[57] obtained equations for different values of N; thus the expressions for $N = 2$ are

$$k_1 = \frac{\bar{n}\,J_2' - \bar{n}J_2}{J_1\,J_2' - J_2'\,J_2} , \quad (28)$$

$$k_2 = \frac{\bar{n}'J_1 - \bar{n}J_1'}{\bar{n}J_2 - \bar{n}'J_2} \quad (29)$$

where

$$J_n = (n - \bar{n})\,[A^-]^n, \quad (30)$$

$$J_n' = (n' - \bar{n}')\,[A^-]'^n . \quad (31)$$

This method has been used by the majority of workers who have investigated the metal complexes of hydroxamic acids[58–62].

If $K_1 \gg K_2$, it is possible to obtain a plot of $\bar{n}$ against $[A^-]$ and find from the latter the stability constants at half-integral values of $\bar{n}$:[63]

$$\bar{n} = 1/2,\ k_1 = 1/[A^-]; \quad (32)$$

$$\bar{n} = 3/2,\ k_2 = 1/[A^-]; \quad (33)$$

$$\bar{n} = 1,\ \sqrt{k_1k_2} = k = 1/[A^-]. \quad (34)$$

Other methods for the calculation of the constants have been summarised by Beck[53]. The most important is the method according to which the relation between $\bar{n}$ and $[A^-]$ is transformed in such a way that the plot of $\bar{n}/(1 - \bar{n})[A^-]$ against $(2 - \bar{n})[A^-]/(1 - \bar{n})$ is represented by a straight line which makes an intercept on the ordinate axis equal to k_1 and which has a slope equal to k_1k_2.

Agrawal et al.[64] developed a computer program based on the method of least squares and using all experimental data.

VIII. LINEAR FREE ENERGY RELATIONS

The standard free energy of reaction ΔF° can be represented as a function of a large number of independent variables w, x, y, and z, whereupon ΔF° is described by the equation

$$d(\Delta F^0) = (\partial \Delta F^0/\partial w)_{x,y,z}\, dw + (\partial \Delta F^0/\partial x)_{w,y,z}\, dx + \ldots \quad (35)$$

An expression whereby the standard free energies of related reactions can be compared has been obtained from Eqn. (35) by regarding $d(\Delta F^\circ)$ as a function of independent variables. Wells[65] used this approximation to derive empirical equations of the Hammett type. Equations involving the metal complex stabilisation factor have also been obtained[66] by regarding the free energy of formation of the complex as a function of a single variable. However, Nieboer and McBryde[67] believe that the standard free energy of formation of metal complexes in a series of reactions is a function of two variables; their reasoning is examined below.

We assume that only a 1 : 1 complex is formed and the following equations are formulated:

$$M + A \overset{K_{MA}}{\rightleftharpoons} MA \quad , \quad (36)$$

$$M_s + A_o \overset{K_{M_sA_o}}{\rightleftharpoons} M_sA_o \quad . \quad (37)$$

$$\Phi = \lg (K_{MA}/K_{M_sA_o}), \quad (38)$$

$$M_s + A \overset{K_{M_sA}}{\rightleftharpoons} M_sA \quad , \quad (39)$$

$$\sigma = \lg (K_{M_sA}/K_{M_sA_o}) \quad , \quad (40)$$

$$M + A_o \overset{K_{MA_o}}{\rightleftharpoons} MA_o \quad , \quad (41)$$

$$\theta = \lg (K_{MA}/K_{M_sA_o}) \quad . \quad (42)$$

The subscripts s and o refer respectively to the metal and the ligand chosen as reference standards. Furthermore, it is readily seen that σ and θ are logarithms of the equilibrium constants for the following substitution reactions:

$$M_sA_o + A \rightleftarrows M_sA + A_o \quad , \quad (43)$$

$$\sigma = \lg K_A \quad , \quad (44)$$

$$M_sA_o + M \rightleftarrows MA_o + M_s \quad , \quad (45)$$

$$\theta = \lg K_M \quad . \quad (46)$$

We assume that Φ is a function of the dependent variables σ and θ and Eqns. (39) and (41) therefore represent series of reactions to be compared. A series of ligands react with the standard or reference metal M_S via reaction (39). It is next assumed that the parameter σ depends only on the nature of the ligand, which is equivalent to a ligand-dependent contribution to Φ. Eqn. (39) now describes a ligand-dependent standard reaction series and Eqn. (41) represents a metal-dependent standard reaction series. In Eqn. (41) the only variable factor is the metal ion M, and A_O is the standard or reference ligand. The assumption is made that the parameter θ depends only on the nature of the metal ion and that a metal-dependent contribution to Φ corresponds to it. Having made these assumptions, we shall subject them to a critical examination.

The changes in Φ caused by the increase in $d\sigma$ and $d\theta$ can be expressed in a differential form by the formula

$$d\Phi = (\partial\Phi/\partial\sigma)_\theta\, d\sigma + (\partial\Phi/\partial\theta)_\sigma\, d\theta \quad . \quad (47)$$

We denote $(\partial\Phi/\partial\sigma)_\theta$ by B and $(\partial\Phi/\partial\theta)_\sigma$ by C. Since $K_{M_SA_O}$ does not vary for any reaction series, it follows that $d \lg K_{M_SA_O} = 0$. Consequently, $d\Phi = d \lg K_{MA}$, $d\sigma = d \lg K_{M_SA}$, and $d\theta = d \lg K_{MA_O}$ and the quantities B and C can be expressed as follows:

$$B = (\lg K_{MA}/\lg K_{M_sA}), \quad (48)$$

$$C = (\lg K_{MA}/\lg K_{MA_o}). \quad (49)$$

MA can be obtained from M_S and A_O in two ways:

(1) $M_sA_o \rightarrow MA_o \rightarrow MA$;
(2) $M_sA_o \rightarrow M_sA \rightarrow MA$.

In the first procedure integration of Eqn. (47) leads to the expression

$$\Phi = B\sigma + \theta \quad (50)$$

and in the second we have

$$\Phi = \sigma + C\theta. \quad (51)$$

In order that Φ is a function of σ only, it must not depend on θ or it must depend on the ligand alone. Putting

$$\Phi' = \lg (K_{MA}/K_{MA_o}), \quad (52)$$

we obtain

$$\Phi' = \Phi - \theta = B\sigma. \quad (53)$$

When $M_S = H^+$, Eqn. (53) is a Hammett type equation, although the quantity σ involved in it is not equal to the Hammett factor. If Φ, σ, and θ are expressed in terms of the corresponding equilibrium constants, then Eqn. (53) can be written in the following form:

$$\lg K_{MA} = B \lg K_{M_sA} + [\lg K_{MA_o} - B \lg K_{M_sA_o}]. \quad (54)$$

Eqns. (53) and (54) describe the substitution effect. With their aid, it is possible to compare the stabilities of the complexes of two metals (M and M_S) for a series of related ligands A. The series of ligands A (hydroxamic acids) usually consists of the initial reagent and its substituted derivatives. Hence σ is a measure of the effect of substitution of the ligand in the ligand-dependent standard reaction series and Φ' is a measure of this effect in the test reaction.

In order that Φ is a function of θ alone, it must depend solely on the metal ion. Defining a new variable Φ'', i.e.

$$\Phi'' = \lg (K_{MA}/K_{M_sA}), \quad (55)$$

we obtain

$$\Phi'' = \Phi - \sigma = C\theta. \quad (56)$$

Substitution of the corresponding values in Eqn. (56) leads to the expression

$$\lg K_{MA} = C \lg K_{MA_o} + [\lg K_{M_sA} - C \lg K_{M_sA_o}]. \quad (57)$$

With the aid of Eqns. (56) and (57), it is possible to compare the stabilities of the complexes of two ligands (A and A_O) with a series of metal ions M and to describe a quasi-substitution effect. The parameters Φ and Φ'' are a measure of the quasi-substitution effect in the metal-dependent standard reaction series and in the test reaction respectively.

The results of the tests of Eqns. (54) and (57) (Fig. 5) with the aid of data for the reactions of *ortho*-substituted *N*-phenylbenzohydroxamic acids with certain metal ions are summarised in Table 12. The existence of two fundamentally different types of behaviour has been noted[67]. In the first case there is a simultaneous dependence of B on the metal ions and of C on the ligands, and in the second case all the values of B and C are unity regardless of the nature of the metal ion and the ligand. The cause of these differences is still obscure.

Table 12. The values of B for *N*-phenylbenzohydroxamic acids.

Ion	B	r	C. I., %	$-\theta$ *
H^+	1.00	1.00	100	0.00
Cu^{2+}	0.90	1.28	99.3	0.67
Zn^{2+}	0.62	0.99	99.9	3.25
Ni^{2+}	0.56	1.11	99.2	3.76

* Here $\theta = \lg K_{MA} - pK_0$; $M_S = H^+$; A_0 = phenylbenzohydroxamic acid.

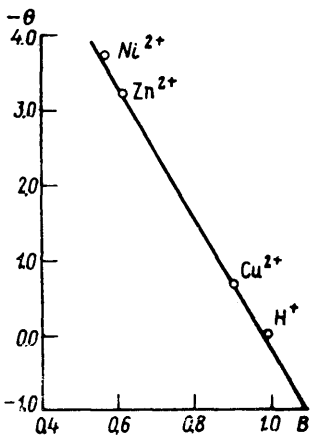


Figure 5. Test of the accuracy for a series of *N*-phenylbenzohydroxamic acids.

IX. THE SOLVENT EFFECT

The stability constants of metal complexes increase with increasing dioxan content. Since the dielectric constant of the medium decreases under these conditions, the ion–ion interaction between the metal ion and the oxygen anion of the ligand intensifies to a greater extent than the ion–dipole interaction between the metal ion and solvent molecules. The plot of $\lg k_1$ against the mole fraction of dioxan for copper(II), zinc(II), nickel(II), and manganese(II) is linear (Fig. 6). According to Irving and Rossotti[68], the dependence of the stability constants of metal complexes of hydroxamic acids in 60% dioxan solution on the stability constants of the metal ions at other dioxan concentrations (50 and 70%) is also linear and the slope of the straight lines is unity (Fig. 6). The same type of dependence has been found in many instances by Van Uitert et al.[69]

X. CORRELATION BETWEEN IONISATION CONSTANTS AND THE STABILITY OF THE COMPLEX

Approximately linear relations between the logarithms of the stability constants of a series of complexes of the same metal ion with a series of closely related ligands have been noted in several studies[68-74]. On this basis, it was expected that more basic ligands should give rise to more stable complexes.

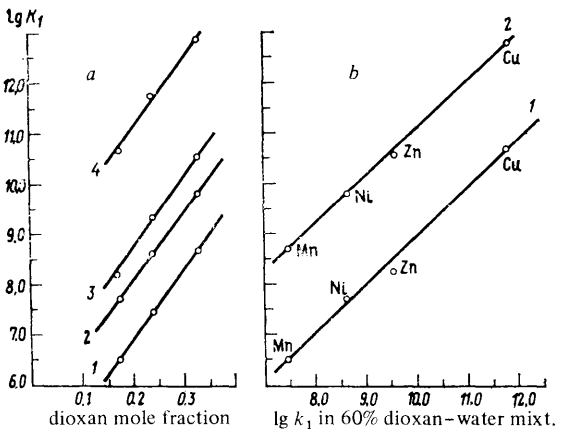


Figure 6. *a*) Dependence of $\lg K_1$ on dioxan concentration [1) Mn^{2+}; 2) Ni^{2+}; 3) Zn^{2+}; 4) Cu^{2+}]; *b*) dependence of $\lg K_1$ in a 60% dioxan–water mixture on $\lg K_1$ in 50% (line *1*) and 70% (line *2*) dioxan–water mixtures (*N*-*m*-tolyl-*m*-methylbenzohydroxamic acid).

If the hydrogen ion is adopted as the standard ion, Eqns. (54) and (57) can be formulated as follows:

$$\lg K_{MA} = B_p K + [\lg K_{MA} - B\,p K_0], \quad (58)$$

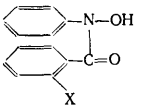
$$\lg K_{MA} = C \lg K_{MA_0} + [pK - C_p K_0]. \quad (59)$$

Eqn. (58) refers to those cases where the stability constants of complexes of one metal ion with a series of ligands substituted in the same position are considered. Eqn. (59) makes it possible to compare the stability constants of complexes of two closely related ligands with a series of metal ions. It has been shown[75] that there is a linear relation between the stability constants and the pK values for copper complexes of *N*-arylhydroxamic acids:

$$\lg K_1 = 0.73\,p K_a + \text{const}. \quad (60)$$

The slope of this straight line is less than unity, which shows that copper(II) has the properties of a π-donor. Agrawal and Tandon[63] showed that the slope of this straight line depends on the nature of the metal ion.

However, in the case of *ortho*-substituted hydroxamic acids (VII) a linear relation between pK_a and $\lg K_1$ was not observed for any metal ion:



(VII)

X=H, CH_3, CH_3O, F, Cl, Br, I, or NO_2 .

Fig. 7 presents typical curves for Cu^{2+}, Zn^{2+}, Ni^{2+}, and Mn^{2+}; evidently the deviations from the straight line are considerable for at least two ligands. The absence of a linear relation can probably be caused by the steric hindrance arising owing to the presence of *ortho*-substituents; electronic effects can also play a role. Such deviations from linearity, due to the perturbing influence of steric hindrance, have been demonstrated for certain types of ligands[68].

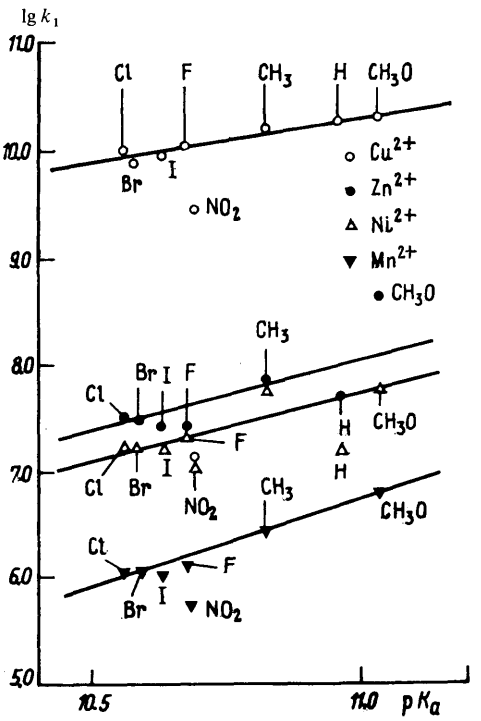


Figure 7. Dependence of $\lg K_1$ on pK_a for *ortho*-substituted *N*-phenylbenzohydroxamic acid derivatives.

The absence of a correlation between pK_a and $\lg K_1$ has been discussed from the standpoint of thermodynamics[73]. The authors established that the linearity of the relation between $\lg K_H(pK_a)$ and $\lg K_{MA}(\lg K_1)$ is not a general property owing to the differences between the ways in which π-donor (or π-acceptor) properties affect pK_a and $\lg K_1$. For beryllium complexes of *para*-substituted hydroxamic acids, the system of linear equations is of the form[76]

$$\lg K_1 = 1.44\, pK_a - 6.99. \qquad (60a)$$

Eqn. (60) has not so far been tested against the stability constants of hydroxamic acids.

XI. THE SEQUENCE OF STABILITY CONSTANTS

The sequence of the stabilities of the copper(II), zinc(II), nickel(II), and manganese(II) complexes of hydroxamic acids can be accounted for by inspecting the ionic radii or the electronegativities determined in terms of the ionisation potentials and ligand field stabilisation energies. The usual stability series for the bivalent ions of 3*d* transition metals, quoted by Maley and Mellor[77] and later by Irving and Williams[78], is

$$Mn^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}.$$

The stability constants of hydroxamic acid complexes can be arranged in the sequence:

$$Mn^{+2} < Ni^{+2} < Zn^{2+} < Cu^{2+}.$$

The dependence of $\lg K_1$ on the atomic number, ΔF°, and ΔH° follows from the above sequence.

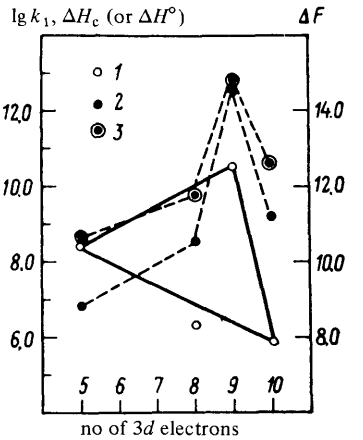


Figure 8. The values of ΔH_C (*1*), ΔF° (*2*), and $\lg K_1$ (*3*) (for *N*-*m*-tolyl-*p*-methylbenzohydroxamic acid) at 25°C in 70% dioxan–water mixtures.

The sequence of the stability constants is the same also in the case of $\lg K_1$ ($\lg K_2$ or $\lg \beta_2$) for hydroxamic acids and bivalent ions of 3*d* transition metals (Fig. 8). Beyond manganese, the constants increase with increasing atomic number, reaching a maximum for $3d^9$ [copper(II)] and then decrease for $3d^{10}$ [zinc(II)]:

$$Mn\ (II) < Ni\ (II) < Cu\ (II) > Zn\ (II)\ .$$

One may note the unusually high stabilities for $3d^9$ [copper(II)], while the stability of $3d^8$ [nickel(II)] is minimal. There is also a correction for the crystal field, which is a maximum for copper and falls rapidly to zero for zinc[79,80]. It is also seen that the stability constants

for zinc(II) are higher than for nickel(II), while those for copper(II) are appreciably higher.

The relative decrease in the stability of nickel(II) chelates may be due to steric hindrance, which prevents the formation of a square planar structure. The same picture was observed also for nickel chelates with other ligands[81,82]. The hydrolysis constants for zinc are lower than those for nickel, which implies a greater affinity of the Zn^{2+} ion for OH groups. Hydroxamic acids containing the –C(O)–N–OH functional group resemble acids with an OH group, because both these groups have a negatively charged oxygen atom. One may expect that, on formation of a bond, the smaller ion (i.e. Zn^{2+}) [83] would give rise to more stable complexes than Ni^{2+}, which is indeed the case.

XII. IONIC CHARGES AND RADII

The stability constants of the metal complexes of hydroxamic acids available at present as a rule increase with increasing ionic potential (i.e. with the charge/radius ratio).

It has been shown[42] that the energy of solution of gaseous ions should be expressed by Eqn. (13) (if it is assumed that they are spherical). Since K is directly related to energy, presumably the ratio of the spherical charge to the radius or to the reciprocal of the radius or the ratio of the charge to the radius should be directly proportional to the stability of the metal chelates with the same ligand. The plot of the stabilities of various metal chelates ($\lg K_1$) against the reciprocals of the ionic radii is linear for all known hydroxamic acids.

XIII. THE IONISATION POTENTIAL AND ELECTRONEGATIVITY

A number of attempts have been made to correlate the stability constants of a series of hydroxamic acid complexes and the ionisation potentials of metals[58–60,63,84,85]. Approximately linear relations have been observed. Other parameters have also been proposed in the literature for correlations. For example, linear relations between $\lg K_1$ and the electronegativities of metal ions X_M (on the Pauling scale) were obtained for the first time by Fernelius and coworkers[86–88] for a series of complexes of a large number of cations with the usual ligands. Normally, individual linear correlations were obtained for univalent, bivalent, and tervalent central metal ions. However, Van Uitert and Fernelius[87] found that a single correlation can be obtained for benzoylmethanates by plotting $\lg K_1$ against the product of X_M and a quantity which was initially referred to as the bond strength and was later identified as the ionic charge z.

In order to characterise individual metal ions, Craig and Nyholm[89] proposed the parameter $R = \Sigma I_M(r_M+r_L)/z^2$, where ΣI_M is the sum of the ionisation energies of the metals up to a charge z and r_M and r_L are the ionic radii of the metal and the ligand respectively. A numerical correlation index Q has been introduced[90]:

$$Q = (a\delta z X_M + b X_M^2)/(a+b) , \qquad (61)$$

where X_M is the Albert electronegativity[57] of the metal ion, a and b are integral weight coefficients (0, 1, 2, ...), and δ is a parameter calculated with the aid of Slater atomic shielding constants[92] and designed to compensate the marked increase of the electronegativities of certain elements due to the small size of their atoms or the marked covalent nature of their bonds. For certain metal ions, the set of parameters a, b, and δ depends on the type of ligand with which the metal forms a complex. Nieborer and McBryde[90] obtained linear relations between $\lg K_1$ and Q for complexes of different metals with more than thirty ligands.

Fig. 9 presents plots of the stability constants of metal complexes of hydroxamic acids against the ionisation potentials of the metal ions. Evidently straight lines were obtained in all cases. The points corresponding to the copper(II) complexes of all the ligands do not fit on these lines and are always above them. The high stability constants of the copper complexes can be accounted for[58–60] by the unusual electronic configuration of the Cu^{2+} ion, for which there is a possibility of additional stabilisation of the complexes due to the tetragonal distortion of the octahedral symmetry as a result of the Jahn–Teller effect. For the Cu^{2+} ion with its d^9 configuration, this distortion is manifested to an appreciable degree.

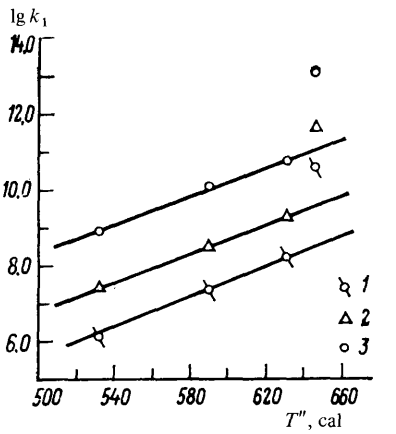


Figure 9. Dependence of $\lg K_1$ (for N-p-tolyl-p-methylbenzohydroxamic acid) on the field ionisation potential I'' in dioxan–water mixtures with different percentages of dioxan: 1) 50; 2) 60; 3) 70.

XIV. THE LIGAND FIELD STABILISATION ENERGY

The stability constants of complexes are related to the free energy change and hence to the temperature-independent heat of reaction:

$$RT\ln K = \Delta F^0 = \Delta H^0 - T\Delta S^0 .$$

These quantities are presented in Fig. 8 and in Tables 13 and 14. The values of $\Delta H_C(\Delta H^\circ)$ for bivalent ions of $3d$ transition metals fit on a curve with a maximum. The latter can be interpreted, as was done above, from the standpoint of ionisation potentials whose curve has a similar shape. The lower line in Fig. 8 represents the same values but with a correction for the orbital stabilisation energy obtained by applying the ligand field theory to the complexes. The curves indicate a constant increase of ΔH_C with increase of the atomic number.

According to the ligand field theory, the thermodynamic properties of metal chelate compounds vary as a function of the inner shells of the transition metal ions and the splitting of the orbitals in the ligand field leads to the stabilisation of the inner electrons compared with the energy which they would have had in the absence of the ligand field[93]. The contraction energy E_r has been determined[94] for a series of transition metals (Mn–Zn) as the heats of the reaction

$$Zn^{2+}_{(g)} + MnA^{2+}_{(aq)} \rightarrow ZnA^{2+}_{(aq)} + Mn^{2+}_{(g)}. \quad (62)$$

E_r can be calculated from the equation

$$E_r = -[\Delta H_H(Zn^{2+}) + \Delta H_c(Zn^{2+})] + [\Delta H_H(Mn^{2+}) + \Delta H_c(Mn^{2+})], \quad (63)$$

where $\Delta H_H(M^{2+})$ is the heat of hydration of the transition metal ion, i.e. the heat of the reaction $M^{2+}_{(g)} = M^{2+}_{(aq)}$, $\Delta H_c(\Delta H^\circ)$ the heat of formation of the complex, and E_r the contraction energy for the series from Mn to Zn ($3d^5$–$3d^{10}$).

Table 13. Free energies, enthalpies, and entropies of formation of complexes of $3d$ transition metal ions and N-m-tolyl-p-methylbenzohydroxamic acid*.

Thermodynamic functions	Dioxan concentration, vol.%								
	50			60			70		
	lg K_1	lg K_2	lg B_2	lg K_1	lg K_2	lg B_2	lg K_1	lg K_2	lg B_2
					Mn^{2+}				
ΔF°	8.87	7.25	16.13	10.17	9.12	19.29	11.81	9.39	21.20
	9.03	7.34	16.37	10.37	9.28	19.65	12.06	2.57	21.63
ΔH°	4.20	4.20	8.40	4.20	2.52	8.40	4.20	2.52	8.40
$-\Delta S^\circ$	15.66	10.16	25.93	20.02	22.14	39.88	25.52	23.04	42.93
	15.69	10.19	25.72	20.02	22.25	36.50	25.50	22.87	42.92
					Ni^{2+}				
ΔF°	10.52	9.02	19.59	11.74	9.15	20.89	13.38	10.78	24.16
	10.74	9.30	20.04	12.01	9.37	21.38	13.69	11.06	24.74
ΔH°	4.20	2.52	6.31	4.20	2.52	6.31	4.20	2.52	6.31
$-\Delta S^\circ$	21.20	25.36	44.54	25.29	22.20	48.90	30.79	27.70	53.16
	21.22	21.99	44.54	25.34	22.22	48.89	30.78	27.70	59.82
					Cu^{2+}				
ΔF°	14.56	12.08	26.70	16.01	15.45	29.56	17.54	15.08	32.62
	14.92	12.26	27.19	16.42	13.67	30.09	16.59	15.37	31.96
ΔH°	3.79	6.72	10.51	3.79	6.72	10.52	3.79	6.72	10.51
$-\Delta S^\circ$	36.12	17.94	54.30	40.99	22.57	63.76	46.18	28.04	74.12
	35.03	17.94	54.11	40.97	22.55	63.51	41.52	28.06	69.58
					Zn^{2+}				
ΔF°	11.19	9.17	20.37	12.71	10.69	23.40	14.34	12.33	26.67
	11.51	9.34	20.85	13.08	10.91	23.99	14.77	12.60	27.37
ΔH°	1.68	4.20	5.89	1.68	4.20	5.89	1.68	4.20	5.89
$-\Delta S^\circ$	31.86	20.02	48.57	36.99	21.77	58.72	42.46	27.27	69.70
	31.89	16.67	48.53	26.98	21.77	58.72	42.46	27.25	69.68

*Here ΔF° and ΔH° are expressed in kcal mole^{-1} and ΔS° is expressed in cal mole^{-1} K^{-1}; the first value refers to 25 °C and the second to 35 °C.

The ligand field stabilisation energy δH for complexes of $3d^n$ transition metal ions M^{2+} can be obtained knowing the enthalpy if one assumes that all the complexes of metal ions ranging from Mn^{2+} to Zn^{2+} have the same symmetry, namely octahedral or tetrahedral[94]. Then

$$\delta H_i(M^{2+}) = \Delta H_c(M^{2+}) - \left(\frac{n-5}{5}\right)E_r - \Delta H_c(Mn^{2+}) - \Delta H_H(M^{2+}),$$

where n is the number of d electrons.

A plot of $\Delta H_H + \Delta H_c$ against the number of $3d$ electrons in the metal ion for complexes of p-methyl-N-m-tolylbenzohydroxamic acid is presented in Fig. 9. The hydration energies ΔH_H were taken from George and McClure[94]. The stabilisation energy of the complexes δH was calculated as the difference between the true value and the corresponding value obtained from the interpolation curve. The stabilisation energy thus increases from $3d^5$ to $3d^8$ and falls for the $3d^{10}$ ion, following the sequence of increasing field stabilisation energy—it is higher for Ni^{2+} than for Cu^{2+}.[95]

Table 14. The ligand field stabilisation energies for bivalent metal ions (N-m-tolyl-p-methylbenzohydroxamic acid)*.

Transition metal	$3d^n$	ΔH_H	ΔH_c	$\Delta H_H + \Delta H_c$	$(n-5)/5$	δH
Mn(II)	$3d^5$	654.0	8.40	662.40	0	
Ni(II)	$3d^8$	716.0	6.31	722.31	26.75	33.30
Cu(II)	$3d^9$	716.9	10.51	727.41	35.67	29.25
Zn(II)	$3d^{10}$	701.1	5.89	706.99	—	

*The contraction energy for the series from Mn to Zn is E_r(Mn–Zn) = 44.59.

Since the ability of the metal ion to interact with the ligand is proportional to the number of vacant sites, the ratio of the successive stability constants is to some extent determined by statistical factors[51]. For anionic ligands, the Coulombic attraction to Mn^{2+} is greater than for MA^+. The quantity lg K_1 – lg K_2 itself is usually positive[96]. The study of hydroxamic acid complexes established that the difference lg K_1 – lg K_2 is greater than zero for all the systems and lies in the range from 1 to 2.5 (in terms of logarithmic units).

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Mixed Organic Derivatives of Mercury and Silicon

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The methods of synthesis and properties of all types of mixed organic derivatives of mercury and silicon are examined and certain examples of these compounds are quoted.
The bibliography includes 224 references.

CONTENTS

I.	Introduction	964
II.	Compounds containing the Si—Hg bond	964
III.	Compounds containing the Si–$(-C-)_n$–Hg group	968
IV.	Compounds containing the Si–X–Hg (X = O, S, Se, Te, or N) group	972
V.	Compounds containing the Si–$(-C-)_n$–X–Hg group	973
VI.	Complexes of organosilicon compounds with mercury salts	974

I. INTRODUCTION

Among the numerous classes of organosilicon derivatives incorporating other elements [1], organosilicon derivatives of mercury are of particular interest owing to the unusual nature of their structure and reactivity and because of definite prospects for their practical applications.

The chemistry of organosilicon derivatives of mercury was first surveyed in 1966 in a monograph [1]. This book was followed by reviews in which organosilicon derivatives of mercury containing an Si–Hg bond were examined [2-6]. In the last twelve years the chemistry of organosilicon derivatives of mercury has developed so vigorously that it has become necessary to carry out another survey of the extensive structural data accumulated in the world literature. This is in fact the aim of the present review, which deals with studies published up to the middle of 1977.

II. COMPOUNDS CONTAINING THE Si–Hg BOND

Compounds containing an Si–Hg bond constitute the class of organosilicon derivatives of mercury which has been most thoroughly investigated. The presence of these compounds was founded mainly as a result of the investigations of Razuvaev, Vyazankin, Wiberg, and Neuman [2,4-7].

1. Methods of Preparation

The first attempt at the synthesis of organosilicon derivatives of mercury containing the Si–Hg bond was unsuccessful [8]. The reaction of triphenylsilyl-lithium with mercury halides, phenylmercury halides, or diphenylmercury was used for this purpose.

The reaction involving $HgCl_2$ leads to the formation of chlorotriphenylsilane, mercury, Hg_2Cl_2, and hexaphenyldisilane (in 45% yield). When $HgBr_2$ is used, the yield of hexaphenyldisilane increases to 63%. Hg_2Cl_2 reacts similarly. The results have been explained by the exchange reaction

$$R_3SiLi + HgX_2 \rightarrow R_3SiX + [LiHgX] \rightarrow LiX + Hg\ ,$$
$$R_3SiLi + R_3SiX \rightarrow R_3SiSiR_3 + LiX\ .$$

When triphenylsilyl-lithium reacts with phenylmercury bromide or diphenylmercury, the main product is tetraphenylsilane:

$$Ph_3SiLi + PhHgX \rightarrow Ph_4Si + Hg + LiX\ ;\quad X = Br, \text{ or } Ph.$$

In this case it was necessary to postulate that an unstable phenyl(triphenylsilyl)mercury salt is formed as an intermediate:

$$Ph_3SiLi + PhHgX \rightarrow Ph_3SiHgPh + LiX\ ,$$
$$Ph_3SiHgPh \rightarrow Ph_4Si + Hg\ .$$

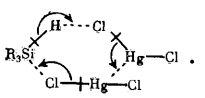
The most convenient method for the synthesis of organosilicon derivatives of mercury containing the Si–Hg bond was discovered in 1964 by Vyazankin and Razuvaev [9]. It is based on the interaction of triorganylsilanes with dialkylmercury derivatives. It had been known previously that the reaction of triorganylsilanes with mercury salts proceeds as a reduction process [9,10-19]:

$$R_3SiH + 2HgX_2 \rightarrow R_3SiX + Hg_2X_2 + HX$$

or

$$R_3SiH + HgX_2 \rightarrow R_3SiX + Hg + HX\ .$$

The intermediate formation of a six-membered cyclic complex in this reaction was postulated:



The reduction to univalent or metallic mercury is determined by the nature of the anion X and the solvent employed. In the reaction of triorganylsilanes with organylmercury halides the latter are also reduced [20]:

$$R_3SiH + R'HgCl \rightarrow R_3SiX + HR' + Hg\ .$$

In contrast to this, in the course of the slow reaction of triethylsilane with diethylmercury (117 h at 130-140°C) the products are compounds with the Si–Hg bond [9,21]:

$$Et_3SiH + Et_2Hg \rightarrow Et_3SiHgEt + C_6H_6\ , \quad (1)$$

$$2Et_3SiH + Et_2Hg \rightarrow (Et_3Si)_2Hg + 2C_6H_6\ . \quad (2)$$

Together with ethyl(triethylsilyl)mercury, one obtains bis(triethylsilyl)mercury, albeit in a low yield (~ 3%), possibly as a result of symmetrisation (disproportionation):

$$2Et_3SiHgEt \rightarrow (Et_3)_2Hg + HgEt_2 .$$

Indeed, when ethyl(triethylsilyl)mercury is heated for 11 h at 170°C, it is converted to a fairly large extent (70%) into bis(triethylsilyl)mercury. The low yields of triethylsilyl derivatives of mercury in reactions (1) and (2) can be explained by their secondary decomposition processes, which is indicated by the high content of metallic mercury in the reaction products[9].

Trichlorosilane reacts slowly with diethylmercury at 20°C for several days, forming ethyl(trichlorosilyl)mercury in 71.8% yield[22,23]. Bis(trichlorosilyl)mercury, which is also formed in this reaction, is a product of the symmetrisation of $EtHgSiCl_3$. Very pure $(Cl_3Si_2)Hg$ can be obtained by the ultraviolet irradiation of a mixture of bis(trimethylsilylmethyl)mercury and trichlorosilane[23]:

$$(Me_3SiCH_2)_2Hg + 2HSiCl_3 \rightarrow 2Me_4Si + Cl_3SiHgSiCl_3 .$$

In the analogous reaction of Me_3SiHCl_2 or $(Me_3)_2SiHCl$ the products are $(Cl_2MeSi)_2Hg$ and $(ClMe_2Si)_2Hg$ respectively, which decompose spontaneously above −79°C with liberation of mercury and substituted disilanes[23]. However, the reactions of $ClMe_2SiH$ and Cl_2MeSiH with di-(t-butyl)mercury at 85°C gave rise to bis(chlorodimethylsilyl)- and bis(dichloromethylsilyl)mercury, which are thermally stable (they sublime *in vacuo* at 80°C).[24] The difficulties experienced by earlier workers[23] can probably be accounted for by the use of radiation, which decomposes these compounds.

When triorganylsilanes interact with di-(t-butyl)mercury[25] or dibenzylmercury[26], the corresponding organosilicon derivatives of mercury, containing the Si–Hg bonds, are formed under mild conditions and in high yields.

The nature of the substituents at the silicon atom in triorganylsilanes affects not only the reactivity of the latter, but also the stability of the organosilicon derivatives of mercury obtained from them. Thus pentaethyldisilane reacts with diethylmercury more vigorously than does triethylsilane[27]. The yield of mono- and di-substituted pentaethyldisilyl derivatives of mercury is higher than that of the analogous triethylsilyl derivatives.

The reaction of triorganylsilanes with diorganylmercury makes it possible to obtain a wide assortment of compounds containing the Si–Hg bond with various substituents at the silicon atom. $[Me_2(n\text{-}Pr)Si]_2Hg$, $(MeEt_2Si)_2Hg$,[28] $(PhMe_2Si)_2Hg$, $(Ph_2MeSi)_2Hg$, $(Ph_3Si)_2Hg$,[29] $[(Me_3SiCH_2)_2Me_2Si]_2Hg$, $[(Me_3Si)_3Si]_2Hg$, $[Me_2(PhCH_2)Si]_2Hg$, and optically active bis(methylphenylsilyl-1-naphthyl)mercury were synthesised by this method. When a 2 : 1 mixture of ethylbis(triethylgermyl)silane and diethylmercury was heated in an evacuated sealed tube (14 h at 150°C), bis[ethylbis(triethylgermyl)silyl]mercury was obtained in 65.9% yield together with ethane[30]. Bis[diethyl(triethylgermyl)silyl]mercury, bis[tris(triethylgermyl)silyl]mercury, and bis[ethylbis(triethylsilyl)]mercury were synthesised under analogous conditions but after more prolonged heating (21–35 h)[30]:

$$2Et_{3-n}(Et_3E)_nSiH + Et_2Hg \rightarrow [Et_{3-n}(Et_3E)_nSi]_2Hg + 2EtH ;$$
$$E = Si \text{ or } Ge;\ n = 1-3 .$$

Ethyltriethylsilylmercury[31] and bis-(*N*-hexamethyldisilazanyl)mercury can be used instead of diorganylmercury[32,33]:

$$Ph_3SiH + EtHgSiEt_3 \rightarrow Ph_3SiHgSiEt_3 + EtH$$
$$\downarrow$$
$$^1/_2(Ph_3Si)_2Hg + ^1/_2(Et_3Si)_2Hg ,$$
$$2(C_6F_5)_3SiH + [(Me_3Si)_2N]_2Hg \xrightarrow{150-170°} 2[(C_6F_5)_3Si]_2Hg + 2(Me_3Si)_2NH .$$

The attempt to use the Wurtz reaction for the synthesis of disilane derivatives by treating halogenotrimethylsilanes with liquid sodium amalgam led to the formation of bis(trimethylsilyl)mercury[7]:

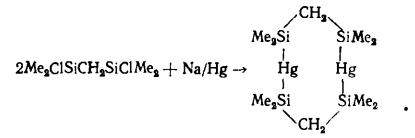
$$2Me_3SiX + 2Na + Hg \rightarrow (Me_3Si)_2Hg + 2NaX ;$$
$$X = Cl \text{ or } Br.$$

The analogous reaction with bromodimethylsilane apparently leads to the formation of $Hg(SiMe_2H)_2$, but this compound could not be isolated because of its instability[7].

Chlorodimethyl(pent-4-en-1-yl)silane gives rise to the corresponding mercury derivative[34]:

$$2H_2C{=}CH(CH_2)_3Me_2SiCl + Na/Hg \rightarrow Hg[SiMe_2(CH_2)_3CH{=}CH_2]_2 .$$

$[CH_2 = CHCH_2Me_2Si]_2Hg$, $(EtMe_2Si)_2Hg$, and $(Et_3Si)_2Hg$ were obtained similarly[28]. The interesting heterocyclic compound 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclo-octane is formed from 2,4-dichloro-2,4-dimethyl-2,4-disilapentane (20°C, 1 month)[35]:



Bis(triphenylsilyl)mercury has been obtained in a yield up to 70% by treating with mercury acetate the ternary complex of ethylbis(triphenylsilyl)aluminium with lithium bromide and tetrahydrofuran (THF)[36]:

$$2Ph_3SiAl(Et)SiPh_3 \cdot 2LiBr \cdot 2THF + 3Hg(OAc)_2 \rightarrow 2(Ph_3Si)_2Hg + Et_2Hg + 2Al(OAc)_3 +$$
$$+ 4LiBr + 4THF.$$

The reaction of bis(trimethylsilyl)mercury with bromosilane (SiH_3Br) makes it possible to obtain silyl(trimethylsilyl)mercury[37]:

$$(Me_3Si)_2Hg + BrSiH_3 \rightarrow Me_3SiHgSiH_3 + Me_3SiBr .$$

$(SiH_3)_2Hg$ and $Me_3SiHgGeH_3$ have been obtained similarly.

2. Physical Properties

According to X-ray diffraction, the $(R_3Si)_2Hg$ molecule has a linear structure, the Si–Hg bond length amounting to 2.500 ± 0.005 Å.[38] The infrared spectra of compounds of this type show an intense absorption band with $\nu_{as}(Hg\text{–}Si)$ = 318 cm^{-1} and $\nu_S(Hg\text{–}Si)$ = 312 cm^{-1}.[7,38] The 474 cm^{-1} frequency corresponds to the stretching vibration of the Hg–C bond in the spectra of compounds of the type $R_3SiHg\text{–}R'$.[39]

The presence of a mercury atom at the silicon atom increases the $\nu(Si\text{–}C)$ frequency[40,41]. Thus $\nu_S(Si\text{–}C)$ = 569 cm^{-1} for hexamethyldisilane and 583 cm^{-1} for bis(triethylsilyl)mercury. This is apparently associated with the greater electronegativity of the $-Hg\text{–}Si(Et)_3$ fragment compared with $-SiEt_3$. When $(Et_3Si)_2$ is replaced by $(Et_3Si)_2Hg$, a new long-wavelength maximum (335 nm) appears in the electronic absorption spectra[42].

The ^1H NMR[43–46] and ^{199}Hg NMR[46] spectra of organosilicon derivatives of mercury of the type R_3SiHgR' and $(R_3Si)_2Hg$ have been investigated. The chemical shift of the protons in the Me_3SiHg group is τ = 9.83 p.p.m. and the spin–spin coupling constant $J(^{199}Hg\text{–}Si\text{–}C\text{–}^1H) = 40.8$ Hz for $(Me_3Si)_2Hg$;[43] τ_{CH_2} = 9.23 p.p.m. and τ_{CH_3} = 8.94 p.p.m. for the Et_3SiHg group in $(Et_3Si)_2Hg$.[44] For asymmetric organosilicon derivatives of mercury of the type Me_3SiHgR,

where R = Me, $CH=CH_2$, $\overline{CH-CH_2-CH_2}$, Ph, or CH_2Ph, the long-range spin–spin coupling constants $J(^{199}Hg-Si-C-^1H)$ increase with increasing electronegativity of the substituent R.[45] They are related to the spin–spin coupling constants for the corresponding organomercury compounds of the MeHgR series by the linear expression $0.453\,J(^{199}Hg-C-^1H) + 6.0 = J(^{199}Hg-Si-C-^1H)$. The existence of this relation shows that the nature of the spin–spin coupling in the two series of compounds is the same.

According to calorimetric data[47], the enthalpy of the Si–Hg bond is $\Delta H^\circ_S(liq.) = 42 \pm 1$ kcal mole^{-1} and its average dissociation energy is $\bar{D} = 20 \pm 3$ kcal mole^{-1}.

In the study of compounds containing the Si–Hg bond mass-spectrometry was used to determine their molecular weights[26,34,48] and only a few communications[28,35,49] have been devoted to their fragmentation. Under electron impact, all the compounds investigated give rise to a molecular ion and subsequently undergo fragmentation with ejection of mercury either as a result of electron impact or in consequence of pyrolytic decomposition[28]. Between 1 and 6% of the overall ionic current corresponds to the molecular ion, amounting to 15.6% only for bis(trimethylsilyl)mercury. The mass spectrum of the latter involves a considerable contribution of three ions containing mercury and silicon: $Me_5Si_2Hg^+$ (5.5%), Me_3SiHg^+ (2.16%), and Me_2SiHg^+ (0.38%). On partial or complete replacement of methyl groups by higher alkyl groups (ethyl and n-propyl), the concentration of ions containing the Si–Hg bond decreases significantly. This is also observed on passing from $(Me_3Si)_2Hg$ to $(Me_2PhSi)_2Hg$. The $(MePh_2Si)_2Hg$ and $(Ph_3Si)_2Hg$ ions, which contain the Si–Hg bond, have not been detected in the mass spectra with the exception of the molecular ions. The replacement by the alkenyl groups $CH_2=CH(CH_2)_n$ ($n = 1-3$) leads to a decrease of the concentration of the molecular ions and to the absence of other ions with the Si–Hg bond, which indicates a destabilising effect of the alkenyl groups on this bond.

Successive substitution of the methyl groups in $(Me_3Si)_2Hg$ by chlorine atoms entails an increase of the concentration of ions with the Si–Hg bond, which shows that the presence of chlorine atoms at the silicon atom stabilises the Si–Hg bond[28].

Under electron impact, 2,2,4,4,6,6,8,8-octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclo-octane gives rise to a molecular ion and ions corresponding to the successive loss of one or two mercury atoms[28,35].

3. Chemical Properties

Organosilicon derivatives of mercury containing the Si–Hg bond are highly reactive. The vast majority of the chemical reactions lead to the cleavage of the covalent Si–Hg bond with preservation of the R_3Si- fragments. On the other hand, these compounds are fairly stable and usually can be vacuum distilled in the absence of atmospheric oxygen without appreciable decomposition. The thermal stability of pentaethyldisilyl derivatives of mercury is higher than that of the analogous triethylsilyl derivatives[27]. Bis(tribenzylsilyl)mercury is also very stable[50,51]. Metallic mercury and the corresponding hexaorganyldisilane are formed quantitatively in the thermal decomposition of bis(triorganylsilyl)mercury[7,22,23]:

$$(R_3Si)_2Hg \rightarrow (R_3Si)_2 + Hg .$$

The thermal decomposition of bis(trimethylsilyl)mercury in solution proceeds via a free-radical mechanism[26,52–55]. The $Me_3Si^\cdot$ radicals formed can not only dimerise to hexamethyldisilane but can also react with the solvent. In aromatic solvents (benzene, toluene, and anisole) this leads to aromaric homolytic substitution products[56–59].

All the compounds containing the Si–Hg bond are sensitive to light. Photolysis of bis(trimethylsilyl)mercury leads to the formation of mercury and $Me_3Si^\cdot$ radicals. The very short-lived $Me_3SiHg^\cdot$ radicals have been identified together with the above species[9,60–62]:

$$(Me_3Si)_2Hg \rightarrow Me_3Si^\cdot + {}^\cdot Hg-SiMe_3 \rightarrow Hg + 2Me_3Si^\cdot$$
$$Me_3Si^\cdot + Hg(SiMe_3)_2 \rightarrow Hg + (Me_3Si)_2 + {}^\cdot SiMe_3 .$$

Compounds with the Si–Hg bond are very readily oxidised by atmospheric oxygen. Oxidation of ethyl(triethylsilyl)mercury is a free-radical chain process initiated at the beginning by the $Et_3SiHg^\cdot$ and $Et_3Si^\cdot$ radicals formed[9,25,63,64]:

$$2R_3SiHgR \rightarrow R_2Hg + R_3SiHg^\cdot + R_3Si^\cdot ,$$
$$R_3Si^\cdot + O_2 \rightarrow R_3SiOO^\cdot ,$$
$$R_3SiHg^\cdot \rightarrow R_3Si^\cdot + Hg ,$$
$$R_3SiOO^\cdot + R_3SiHgR \begin{cases} \rightarrow R_3SiOHgR + R_3SiO^\cdot \\ \rightarrow (R_3SiO)_2 + RHg^\cdot \end{cases} ,$$
$$R_3SiO^\cdot + R_3SiHgR \rightarrow (R_3Si)_2O + RHg^\cdot ,$$
$$RHg^\cdot + O_2 \rightarrow CH_3CHO + {}^\cdot HgOH ,$$
$$^\cdot HgOH + R_3SiHgR \rightarrow R_3SiOH + RHg^\cdot + Hg^\cdot ,$$
$$2R_3SiOH \xrightarrow[-H_2O]{} (R_3Si)_2O ;$$
$$R=Et .$$

The oxidation is accelerated severalfold in the presence of traces of Lewis bases capable of forming complexes with organomercury compounds, (ammonia, amines, triphenylphosphine, etc.)[64–66].

Under the usual conditions, bis(triorganylsilyl)mercuranes $(R_3Si)_2Hg$ are resistant to hydrolysis and alcoholysis, but these reactions take place readily in a homogenising solvent. Thus, when bis(triphenylsilyl)mercury is acted upon by moist benzene, there is very rapid formation of mercury (quantitative), triphenylsilanol, and hydrogen[26]:

$$\begin{array}{l} Ph_3Si-Hg-SiPh_3 \\ \quad\vdots\quad\vdots \\ \quad HO-H \end{array} \rightarrow Ph_3SiOH + HHgSiPh_3 ,$$
$$HHgSiPh_3 + H_2O \rightarrow Ph_3SiOH + [H_2Hg] \rightarrow H_2 + Hg + Ph_3SiOH .$$

In addition, small amounts of triphenylsilane, hexaphenyldisiloxane, and hexaphenyldisilane are produced. The alcoholysis of $(R_3Si)_2Hg$ can proceed via two pathways[67]:

$$\begin{array}{l} Ph_3Si-Hg-SiPh_3 \\ \quad\vdots\quad\vdots \\ \quad RO-H \end{array} \rightarrow Ph_3SiOR + HHgSiPh_3 \rightarrow Ph_3SiOR + Hg + HSiPh_3 ,$$
$$\begin{array}{l} HHg-SiPh_3 \\ \quad\vdots\quad\vdots \\ \quad H\ -OR \end{array} \rightarrow Ph_3SiOR + [H_2Hg] \rightarrow Ph_3SiOR + H_2 + Hg ,$$
$$\begin{array}{l} Ph_3Si-Hg-SiPh_3 \\ \quad\vdots\quad\vdots \\ \quad HO-R \end{array} \rightarrow Ph_3SiOH + RHgSiPh_3 .$$

The interaction of organosilicon derivatives of mercury containing the Si–Hg bond with acids leads to the quantitative formation of mercury and can serve as a method for the analysis of these compounds[7,25,50]:

$$(R_3Si)_2Hg + HX \rightarrow R_3SiH + Hg + R_3SiX ;$$
$$R=Me,\ Et\ or\ Ph;\ X=Cl\ or\ OAc .$$

Bis(trimethylsilyl)mercury reacts with CO_2 only in hexamethylphosphoramide (HMPT) to form CO and hexamethyldisiloxane[68]:

$$(Me_3Si)_2Hg + CO_2 \xrightarrow[-Hg]{} \begin{array}{l} SiMe_3 \\ | \\ O=C-OSiMe_3 \end{array} \rightarrow (Me_3Si)_2O + CO .$$

The reaction with carbon disulphide proceeds via a similar mechanism:

$$(Me_3Si)_2Hg + CS_2 \xrightarrow{-Hg} S{=}C(SiMe_3){-}SSiMe_3 \rightarrow (Me_3Si)_2S + 1/n\,(CS)_n .$$

The interaction of SO_2 with bis(trimethylsilyl)mercury at 20°C proceeds via the mechanism[68]

$$(Me_3Si)_2Hg + SO_2 \xrightarrow{-Hg} Me_3Si{-}O{-}S{-}O{-}SiMe_3 .$$

The bis(trimethylsilyl)sulphoxylate formed decomposes at room temperature into hexamethyldisiloxane and sulphur, which reacts with mercury to form HgS.

Acyl peroxides (but not t-butyl peroxide[2]) react vigorously with compounds containing the Si–Hg–Si[2,25,69] or Si–Hg–C[9] groups:

$$(Et_3Si)_2Hg + (PhCOO)_2 \rightarrow Hg + 2Et_3SiOCOPh ,$$
$$2Et_3SiHgEt + (PhCOO)_2 \rightarrow Et_2Hg + 2PhCOOSiEt_3 + Hg .$$

Aliphatic aldehydes interact with bis(trimethylsilyl)mercury very slowly in benzene. On the other hand, aromatic aldehydes interact rapidly even at 20°C, forming bis(trimethylsiloxy)hydrobenzoin[70,71]:

$$(Me_3Si)_2Hg + 2RCHO \xrightarrow{-Hg} R{-}CH(OSiMe_3){-}CH(OSiMe_3){-}R ,$$

where **R** = aryl.

2,2-Dichlorovinyloxytrimethylsilane is formed from chloral via an exothermic reaction[71]:

$$(Me_3Si)_2Hg + CCl_3CHO \xrightarrow{-Hg} Me_3SiOCHCCl_3 \rightarrow Me_3SiCl + Me_3SiOCH{=}CCl_2 .$$
($SiMe_3$ on the CHCCl$_3$ carbon)

Bis(trimethylsilyl)mercury reacts vigorously at room temperature with ketones and quinones such as acetone[72-74], hexafluoroacetone[75], cyclohexanone[72,73], 9-fluorenone[76], acetophenone[70,72,73], benzophenone[72,73], 1,4-naphthoquinone, 1,2-naphthoquinone, and anthraquinone[70], forming the intermediate $R_2COSiMe_3$ radical, which then dimerises or disproportionates:

$$(Me_3Si)_2Hg + R_2CO \xrightarrow{-Hg} R{-}C(R)(OSiMe_3){-}\cdot \rightarrow R{-}C(R)(OSiMe_3){-}H + RCH{=}C(R)(OSiMe_3)$$
$$\rightarrow R{-}C(R)(OSiMe_3){-}C(R)(OSiMe_3){-}R .$$

1,2-Diketones react via the mechanism[71]

$$(Me_3Si)_2Hg + RCOCOR \xrightarrow{-Hg} R{-}C(OSiMe_3){=}C(OSiMe_3){-}R ,$$

where **R** = Me or Ph.

The following reactions occur when bis(trimethylsilyl)-mercury interacts with diorganylketones[68,70]:

$$(Me_3Si)_2Hg + 2R_2C{=}C{=}O \xrightarrow{-Hg} R_2C(SiMe_3){-}CO{-}C(OSiMe_3){=}CR_2 ,$$
$$R_2C{=}C(OSiMe_3){-}CR_2{-}COSiMe_3 ,$$
$$R_2C{=}C(OSiMe_3){-}C(OSiMe_3){=}CR_2 .$$

where **R** = Me or Ph.

The reaction with aryl isocyanates in HMPT leads to the formation of *N*,*N'*-diaryl-*N*,*N'*-bis(trimethylsilyl)urea and carbon monoxide[68,70]:

$$(Me_3Si)_2Hg + 2R{-}N{=}C{=}O \xrightarrow[-Hg]{-CO} R{-}N(Me_3Si){-}C(=O){-}N(SiMe_3){-}R ,$$

where **R** = Ph, 4-$CH_3C_6H_4$, or 1-$C_{10}H_7$.

Diphenylcarbodiimide reacts rapidly[68] with bis(trimethylsilyl)mercury in HMPT via the mechanism

$$(Me_3Si)_2Hg + PhN{=}C{=}NPh \xrightarrow{-Hg} Ph{-}N(SiMe_3){-}C{=}NPh .$$

1,4- and 1,6-additions take place in the reaction of bis(trimethylsilyl)mercury with maleate or fumarate esters[71,78]:

$$(Me_3Si)_2Hg + \begin{matrix}HC{-}COOEt\\ \|\\ HC{-}COOEt\end{matrix} \xrightarrow{-Hg} \begin{matrix}HC(OSiMe_3){=}C{-}OEt\\ |\\ HC{-}SiMe_3\\ |\\ COOEt\end{matrix} + \begin{matrix}HC(OSiMe_3){=}C{-}OEt\\ |\\ HC{=}C{-}OEt\\ |\\ OSiMe_3\end{matrix} .$$

On heating or under ultraviolet irradiation, bis(trimethylsilyl)mercury cleaves the isoxazole ring[79]:

$$6\,(Me_3Si)_2Hg + 2N{=}CRCH{=}CR'O \xrightarrow{-3Hg} [(Me_3Si)_2NCR{=}CHCR'OSiMe_3]_2 ;$$
R, R'=H or Me.

The reaction of bis(trimethylsilyl)mercury with pyridine and its derivatives leads to *N*,*N'*-bis(trimethylsilyl)tetrahydro-4,4'-bipyridyls[80,81-83]:

$$(Me_3Si)_2Hg + 2N{=}C_5H_4(X) \xrightarrow{-Hg} Me_3SiN(X){-}(X)C_5H_4NSiMe_3 ;$$
X=H, 2-Me, 3-Me, 3-CN, 3-COOMe, 4-COOMe, or 4-Ac.

When an equimolar mixture of $(Me_2Si)_2Hg$ and a pyridine derivative containing the carbonyl group in the 4-position is irradiated with ultraviolet light, the α-trimethylsiloxy-*N*-trimethylsilyl derivatives of 4-methylenedihydropyridines are formed[84]:

$$(Me_3Si)_2Hg + N{=}C_5H_4{-}C(=O)R \xrightarrow{-Hg} Me_3SiN(H){-}C(OSiMe_3){=}CR ;$$
R=H, Me, or Ac.

Bis(trimethylsilyl)mercury reacts with azo-compounds as a nucleophile, adding to the azo-group[78,82]:

$$(Me_3Si)_2Hg + R{-}N{=}N{-}R \rightarrow R{-}N(HgSiMe_3){-}N(SiMe_3){-}R \xrightarrow{-Hg} R{-}N(SiMe_3){-}N(SiMe_3){-}R ;$$
R=EtOCO, Ph, or 2-C_5H_4N.

$(Me_3Si)_2Hg$ interacts with aryl azides via a radical mechanism to form nitrogen and *N*,*N'*-bis(trimethylsilyl)-anilines[68]:

$$(Me_3Si)_2Hg + R{-}N{=}N{-}N \xrightarrow{-Hg} (Me_3Si)_2N{-}N{=}NR \xrightarrow{-N_2} (Me_3Si)_2NR ;$$
R=Ar .

The reaction of t-butyl(trimethylsilyl)mercury with substituted benzylidenemalonodinitriles leads to *N*-trimethylsilylketenimines[85]:

$$Me_3SiHgCMe_3 + XC_6H_4CH{=}C(CN)_2 \rightarrow XC_6H_4CH(CMe_3)C(CN){=}C{=}NSiMe_3 ;$$
X=H, Me, MeO, Cl, or NO_2.

t-Butyl(trimethylsilyl)mercury adds to 4-$MeOC_6H_4CH{=}C(CN)COOEt$ to form *O*-silylketen acetal[85].

In the interaction of bis(trimethylsilyl)mercury with an olefin under the conditions of photolysis trimethylsilyl radicals add to the double bond[86]:

$$(Me_3Si)_2Hg + CH_3CH(CH_3)CH{=}CHCH_3 \xrightarrow{-Hg} CH_3CH(CH_3)\underset{Me_3Si}{CH}{-}\underset{SiMe_3}{CH}CH_3 .$$

The attempts to achieve the transfer of the trimethylsilyl radical from $(Me_3Si)_2Hg$ to zinc or aluminium were unsuccessful[7]. Bis(trimethylsilyl)mercury interacts with zinc only at a high temperature, liberating dimethylmercury. The interaction with aluminium results in the liberation of metallic mercury and the formation of a mixture of compounds not containing the Si–Al bond. On the other hand, lithium reacts with bis(triethylsilyl)mercury and ethyl(triethylsilyl)mercury in THF with formation of triethylsilyl-lithium[87,88]:

$$(Et_3Si)_2Hg + 2Li \rightarrow Hg + 2Et_3SiLi ,$$
$$Et_3SiHgEt + 2Li \rightarrow Hg + Et_3SiLi + EtLi .$$

This reaction is convenient for the synthesis of Alk_3SiLi.

Bis dimethyl(pent-4-en-1-yl)silyl mercury reacts with lithium to form the corresponding lithio-derivative which cyclises and gives rise to 1,1,2-trimethyl-1-silacyclopentane after hydrolysis[34]:

$$(CH_2{=}CHCH_2CH_2CH_2Me_2Si)_2Hg + Li \xrightarrow{-Hg} 2CH_2{=}CHCH_2CH_2CH_2Me_2SiLi \rightarrow$$
$$\rightarrow \underset{Me\quad Me}{\overset{}{Si}}{-}CH_2Li \xrightarrow{H_2O} \underset{Me\quad Me}{\overset{}{Si}}{-}CH_3 .$$

The reaction of $(Et_3Si)_2Hg$ with metallic potassium or sodium in an aromatic solvent results in the formation of triethylsilylpotassium and triethylsilylsodium, but the reaction with the solvent predominates in this case[89]: it may be that Et_3SiM is a reaction intermediate, which interacts with the solvent to form Et_3SiPh and MH:

$$(Et_3Si)_2Hg + 2M \xrightarrow{C_6H_6} 2Et_3SiM + Hg ,$$
$$Et_3SiM + C_6H_6 \rightarrow Et_3SiH + PhM ,$$
$$PhM + Et_3SiH \rightarrow PhSiEt + M ;$$
M = K or Na.

Triethylsilylpotassium can be obtained by treating $(Et_3Si)_2Hg$ with potassium using triethylsilane as a solvent[89].

Bis(trimethylsilyl)mercury interacts with alkali metals in 1,2-dimethoxyethane, forming dimetallo-organosilicon complexes[90,91]:

$$2(Me_3Si)_2Hg + 2M \rightarrow (Me_3Si)_4HgM_2 + Hg ;$$
M = K or Na.

The analogous lithium compounds have been obtained by the direct interaction of bis(trimethylsilyl)mercury with Me_3SiLi:

$$(Me_3Si)_2Hg + Me_3SiLi \rightarrow (Me_3Si)_2HgLi ,$$
$$(Me_3Si)_2Hg + 2Me_3SiLi \rightarrow (Me_3Si)_4HgLi_2 .$$

The formation of $K_2Hg(SiEt_3)_4$ has been observed in the reaction of bis(triethylsilyl)mercury with potassium cyanide in THF in the presence of a crown-ether[92]:

$$3(Et_3Si)_2Hg + 2KCN \rightarrow (Et_3Si)_4HgK_2 + 2Hg + 2Et_3SiCN .$$

Organosilicon derivatives of mercury containing the Si–Hg bond are capable of exchanging the trialkylsilyl fragment for the anions of a number of metal salts. For example, the interaction with mercury salts proceeds via the general mechanism[92-96]

$$(R_3Si)_2Hg + HgX_2 \rightarrow 2R_3SiX + 2Hg ;$$
X=Cl, Br, I, CN, $Co(CO)_3$, $Cr(CO)_3C_6H_5$, $W(CO)_3C_6H_5$, or $Mo(CO)_3C_5H_5$.

The intermediates in this reaction are probably compounds of the type R_3SiHgX, which immediately decompose to mercury and R_3SiX.

The products of the reaction of bis(triethylsilyl)mercury with alkylmercury chlorides in the absence of a solvent in atmospheric oxygen give rise to the corresponding alkyl(trialkylsilyl)mercuranes together with mercury and a trialkylchlorosilane[61,97-98]:

$$(Et_3Si)_2Hg + RHgX \rightarrow Et_3SiHgR + Et_3SiX + Hg ,$$
R=Me, Et, Pr, iso-Pr, t-Bu; X=Cl .

The reactions of $(R_3Si)_2Hg$ with organomercury compounds of the type HgR'_2, where R′ is a hydrocarbon or a polyfluoro-hydrocarbon radical [Me_2, iso-Pr, $CH{=}CH_2$, Ph,[45] $-C-C-Ph$ (bonded to $B_{10}H_{10}$),[99] CF_3, CH_2CF_3, $CHFCF_3$, CF_2CF_3, $CFClCF_3$, $CH(CF_3)_2$, and $CF(CF_3)_2$[95,100]] in aprotic solvents (benzene, toluene) lead to the corresponding trialkylsilylorganylmercuranes:

$$(Et_3Si)_2Hg + HgR'_2 \rightarrow 2Et_3SiHgR' .$$

$(R_3Si)_2Hg$ reacts via a similar mechanism with dimetallo-organic compounds of the type HgR'_2, where R = $SnMe_3$, $GeMe_3$, or $SiMeCl_2$.[43,49] Other reactions of bis(trialkylsilyl)mercuranes are listed in the Table.

Organosilicon derivatives of mercury containing the Si–Hg bond are used in the synthesis of organosilicon derivatives which are difficult to obtain otherwise and also as catalysts in the polymerisation of styrene[29,135] or ethylene[136] and in the hydroxylation of unsaturated compounds (in combination with ultraviolet irradiation)[137]. However, the considerable lability of the Si–Hg bond limits the scope of the industrial utilisation of compounds of this class.

III. COMPOUNDS CONTAINING THE Si–(–C–)$_n$–Hg GROUP

Compounds containing the Si–(–C–)$_n$–Hg group have been known much longer than those discussed above but have been investigated in much less detail.

1. Methods of Synthesis

(a) Organometallic synthesis. The first compound containing the Si–(–C–)$_n$–Hg group was obtained in 1945 by Whitmore and Sommer[138] by treating trimethylsilylmethylmagnesium chloride with mercury(II) chloride:

$$Me_3SiCH_2MgCl + HgCl_2 \rightarrow Me_3SiCH_2HgCl + MgCl_2 .$$

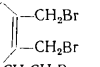
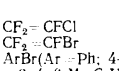
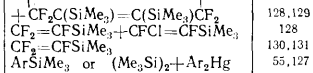
The compounds RHgCl, where R = $Me_3CSiMe_2CH_2$,[139] $PhMe_2SiCH_2$,[140-143] $Me_3SiCHMe$,[144] $Me_3SiSiMe_2CH_2$, $EtMe_2SiSiMe_2CH_2$, or $(Me_3Si)_2CH$,[139] were subsequently synthesised by a similar procedure.

The reaction of 2 moles of Me_3SiCH_2MgCl with 1 mole of $HgCl_2$ leads to the formation of bis(trimethylsilylmethyl)mercury in yields up to 50%:[145,146]

$$2Me_3SiCH_2MgCl + HgCl_2 \rightarrow (Me_3SiCH_2)_2Hg + 2MgCl_2 .$$

Symmetrical organosilicon derivatives of mercury of the type R_2Hg (for the significance of R, see above) have been obtained in the same way.

Reactions of $(R_3Si)_2Hg$ with organic and organometallic compounds.

R_2	Reagent	Reaction product	References
Et_3, $MePh_2$	$Hg[C(N_2)COCH_3]_2$	$R_3SiC(N_2)COCH_3$	101
Et_3, $MePh_2$	$Hg[C(N_2)COOE]_2$	$R_3SiC(N_2)COOEt$	102,103
Et_3	$Hg(CH_2COCH_3)_2$	$Et_3SiOC(CH_3)=CH_2$	104
Me_3	R'_3SnX (X = OMe, OEt, NEt_2, $OSnMe_3$)	$R'_3SnSnR'_3$	50,105,106
Me_3	Me_3GeOMe	$Me_3SiHgGeMe_3$	107
Me_3	$Fe(CO)_5$	$(Me_3Si)_2Fe(CO)_4$	108
Cl_3	$[Mn(CO)_5]_2$	$Cl_3SiMn(CO)_5$	23
Me_3	Me_3Tl	$(Me_3Si)_3Tl$	109
Me_3	$(Et_3P)_2PtCl_2$	$(Et_3P)_2Pt(Cl)SiMe_3$	110,111
Me_3	$[(Ph_2P)_2CH_2]PtCl_2$	$Pt(SiMe_3)_2[(PhP)_2CH_2]$	112–114
Me_3	$Ir(Et_3P)_2(CO)Cl$	$Ir(HgSiMe)(SiMe_3)_2(Et_3P)_2CO$	115
Me_3	$Pb(OAc)_4$	$Me_3SiPb(OAc)_3$	116
Me_3	$(CF_3)_2P(S)Cl$	$Me_3SiSP(CF_3)_2$	117
Me_3	$PhHgCCl_2Br$	$Me_3SiCCl=CCl_2$	118–120
Et_3, iso-Pr_3	S	$R_3SiSHgSiR_3$	50,100
Et_3, iso-Pr_3	Se	$R_3SiSeHgSiR_3$	121–123
Et_3	HSeBu	$Et_3SiSeBu$	124
Me_3	R'X (R = CCl_3, $CHCl_2$, CH_2Cl, Me, Et, iso-Pr, Bu; X = Cl, Br)	Me_3SiHgR	9,25,50, 125–127
Me_3	Ph_3CCl	$(Ph_3C)_2$	127
Me_3			126
Me_3	$BrCH_2CH_2Br$	$CH_2=CH_2$	127
Me_3	BrCH CHBr	CH≡CH	127
Me_3	$CF_3CF=CF_2$	$CF_3CF=CFSiMe_3$	129
Me_3	$CF_3C\equiv CCF_3$	$CF_3C(SiMe_3)=C(SiMe_3)CF_3$	129
Me_3	$CF_3C\equiv CF$	$CF_3C\equiv CSiMe_3 + CF_3C(SiMe_3)=C(SiMe_3)F$	129
Me_3		$CF_2=CFSiMe_3$	128,129
Me_3	$CF_2CF=CFCF_2$		128,129
Me_3	$CF_2=CFCl$	$CF_2=CFSiMe_3 + CFCl=CFSiMe_3$	128
Me_3	$CF_2=CFBr$	$CF_2=CFSiMe_3$	130,131
Me_3	ArBr (Ar = Ph; 4-MeC_6H_4; 2, 4, 6-$Me_3C_6H_3$; 1-naphthyl)	$ArSiMe_3$ or $(Me_3Si)_2 + Ar_2Hg$	55,127
Me_3	C_6F_5Br	$C_6F_5SiMe_3$ or $(Me_3Si)_2 + (C_6F_5)_2Hg$	131,132
Me_3	$(CF_3)_2NCl$	$CF_3N=CF_2$	133,134

The mercuration of Me_3SiCH_3MgCl by organylmercury chlorides R'HgCl leads to compounds of the type Me_3SiCH_2HgR' [R' = Me, n-C_6H_{13}, Ph,[138] $CH_2SiMe_2CMe_3$,[139] CH_2GeMe_3,[147] $CH_2Me_2SiSiMe_3$, $CH_2Me_2SiSiMe_2Et$, or $CH(SiMe_3)_2$ [139]].

Dimethylmercury reacts with trichloromethylsilane or dichlorodimethylsilane at 450°C to form $(Cl_3SiCH_2)_2Hg$ and $(Cl_2CH_3SiCH_2)_2Hg$ respectively [148]:

$$2(CH_3)_nSiCl_{4-n} + (CH_3)_2Hg \rightarrow [(CH_3)_{n-1}Cl_{4-n}SiCH_2]_2Hg + 2CH_4 .$$

These compounds were not isolated in a pure form but were identified as their methyl derivatives, obtained by treatment with methylmagnesium bromide.

Organozinc synthesis can also be used to prepare certain organosilicon derivatives of mercury, for example [149]:

$$2Me_3SiCHIZnI + HgCl_2 \rightarrow (Me_3SiCHI)_2Hg + 2IZnCl .$$

The yield of bis[iodo(trimethylsilyl)methyl]mercury is then 45% (traces of $Me_3SiCHIHgI$ were also found).

The reaction of dichloromethyl(trimethylsilyl)lithium with mercury(II) bromide at 135°C has been used to synthesise dichlorobis(trimethylsilyl)methylmercury, which serves as a source of chlorotrimethylsilylcarbene [150–152]:

$$2Me_3SiCCl_2Li + HgBr_2 \rightarrow (Me_3SiCCl_2)_2Hg + 2LiBr .$$

For an initial reactant ratio of 1 : 1, up to 5% of Me_3SiCCl_2.HgBr is formed together with the symmetrical compound (yield 44%). When $HgBr_2$ is replaced by $HgCl_2$, the yield of $(Me_3SiCCl_2)_2Hg$ falls to 23% and up to 17% of Me_3SiCCl_2.HgCl is formed.

Trimethyl[(methylmercuri)(trimethylsilyl)methylene]-phosphorane has been obtained by the reaction of the lithium derivative of trimethyl(trimethylsilylmethylene)phosphorane with methylmercury chloride [153]:

$$Me_3P(CH_2Li)=CHSiMe_3 + Me_3HgCl \rightarrow Me_3P=C(HgMe)(SiMe_3) + LiCl .$$

(b) Mercuration of unsaturated organosilicon compounds. The addition of mercury salts to the double bonds of unsaturated organosilicon compounds was first achieved in 1959 [154]:

$$Me_3SiCH=CH_2 + Hg(OAc)_2 \xrightarrow[-CH_3COOH]{H_2O} Me_3SiCH(HgOAc)CH_2OH .$$

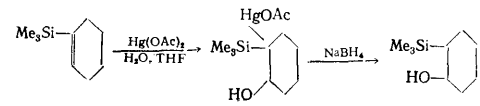
The reduction of the product with sodium amalgam led to (2-hydroxyethyl)trimethylsilane, which confirmed the above anomalous mode of reaction [the mercuration of olefins of the type $RCH=CH_2$ with mercury acetate usually proceeds in accordance with the Markovnikov rule, leading to $RCH(OH)CH_2HgOAc$ [155]]. The unusual mode of mercuration in this case is due to the interaction of the π electrons of the vinyl group with the vacant 3*d* orbitals of the silicon atom (the effect of the $d\pi - p\pi$ conjugation), which predominates over the opposed inductive effect of the trimethylsilyl group, which reduces the electron density at the β-carbon atom.

When trimethylallylsilane is acted upon by mercury salts, only the products of the cleavage at the $Si-CH_2$ bond are formed, which is apparently due to the β-decomposition of the adduct formed initially [156–158]. The study of the kinetics of this process showed that its mechanism does not fit within the framework of simple bimolecular electrophilic substitution [158]. The reaction proceeds in several stages, the rate of the process being determined by the cleavage of the adduct to $(CH_3)_3SiX$ and $CH_2=CHCH_2HgS$.

The addition of bis(trinitromethyl)mercury to trimethylvinylsilane in water, alcohol, benzene, and carbon tetrachloride leads to bis[(3,3,3-trinitro-1-trimethylsilyl)propyl]mercury (in 90% yield) [156,157]:

$$2Me_3SiCH=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow Hg[-CH(SiMe_3)CH_2C(NO_2)_3]_2 .$$

The interaction of mercury acetate with 1-trimethylsilylcyclohexane in an aqueous medium gives rise to an addition product, whose reduction with sodium tetrahydroborate results in the formation of 1-trimethylsilyl-2-cyclohexanol [159]:



The mode of addition of the HgOAc group in the mercuration of unsaturated compounds of the type $RCH=CH(CH_2)_nSiX_3$ (R = H, Me, or Ph; X = Me, Et, Me, Et, or Ac)

depends on the nature of the substituents at the double bond (**R**) and at the silicon atom (**X**) as well as the position of the double bond[160]. It has been established by ^1H NMR that, in the reaction of mercury acetate with trimethylvinylsilane in both alcoholic and acetic acid media, the HgOAc group adds only to the α-carbon atom:

$$Me_3SiCH{=}CH_2 + Hg(OAc)_2 \xrightarrow[-AcOH]{R'OH} Me_3SiCH(HgOAc)CH_2OR';$$
$$R' = Me, \text{ or } Ac.$$

The addition of mercury acetate to trimethylpropenylsilane and trimethyl-β-styrylsilane is no longer selective. In both instances the HgOAc group adds to both α- and β-carbon atoms:

$$Me_3SiCH{=}CHR + Hg(OAc)_2 \xrightarrow[-AcOH]{R'OH} \begin{cases} \rightarrow Me_3SiCH(HgOAc)CH(R)OR' \\ \rightarrow Me_3SiCH(OR')CH(R)HgOAc \end{cases}.$$

The ratio of the α- and β-adducts is 7 : 3 for **R** = Me and 1 : 1 for **R** = Ph. The breakdown of selectivity in the addition reaction is due to the enhanced electron density at the β-carbon atom owing to the $+I$ effect of the methyl group or the incorporation of the phenyl group in the conjugation chain.

Contrary to data published previously[161], the addition of mercury acetate to alkenyltrialkoxysilanes in an alcoholic medium is in all cases quantitative and vigorously selective with formation of α-mercurated adducts alone[160]:

$$(MeO)_3SiCH{=}CHR + Hg(OAc)_2 \xrightarrow{MeOH} (MeO)_3SiCH(HgOAc)CH(R)OMe + AcOH;$$
$$R = H, Me, \text{ or Ph}.$$

On the other hand, only the γ-mercuri-derivative has been obtained from trialkoxyallylsilane:

$$(EtO)_3SiCH_2CH{=}CH_2 + Hg(OAc)_2 \xrightarrow[-AcOH]{EtOH} (EtO)_3SiCH_2CH(OEt)CH_2HgOAc.$$

The adducts formed in both cases are fairly stable.

In nitromethane or chloroform mercury acylates add smoothly to vinylsilanes with formation of the corresponding α-acyloxymercuri-derivatives[160]:

$$X_3SiCH{=}CH_2 + Hg(OCOR)_2 \rightarrow X_3SiCH(HgOCOR)CH_2OCOR;$$
$$X = Et, Me, \text{ or AcO}; R = Me, \text{ or Ph}.$$

When trialkylethynylsilanes are acted upon by mercury salts, the acetylenic hydrogen atom is substituted instead of the addition to the triple bond[162]:

$$Me_3SiC{\equiv}CH + XHgOAc \rightarrow Me_3SiC{\equiv}CHgX + AcOH;$$
$$X = I, \text{ or OAc}.$$

The reaction of mercury(II) chloride with 1-triethylsilyl-2-tripropylstannylethylene leads to the cleavage of the bond between tin and the unsaturated group[163]:

$$Et_3SiCH{=}CHSnPr_3 + HgCl_2 \rightarrow Et_3SiCH{=}CHHgCl + ClSnPr_3.$$

The interaction of methylmercury chloride with trimethyl(trimethylsilylmethylene)phosphorane leads to trimethyl[(methylmercuri)(trimethylsilyl)methylene]phosphorane[153,164]:

$$MeHgCl + Me_3P{=}CHSiMe_3 \rightarrow (Me_3\overset{+}{P}{-}\underset{\displaystyle SiMe_3}{\underset{|}{CH}}{-}HgMe)\,Cl^- \xrightarrow{Me_3P=CHSiMe_3} \rightarrow Me_3P{=}C\begin{matrix}HgMe\\SiMe_3\end{matrix} + (Me_3\overset{+}{P}CH_2SiMe_3)\,Cl^-.$$

(c) The cleavage of sila- and 1,3-disilacyclobutanes with mercury salts. When 1,1-dialkylsilacyclobutanes are acted upon by mercury salts in an aqueous or alcoholic medium, the endocyclic Si–C bond is cleaved[165–168]. This results in the smooth formation of γ,γ'-mercurated 1,1,3,3-tetraorganyl-1,3-dipropylsiloxanes:

$$R_2Si\begin{matrix}CH_2\\CH_2\end{matrix}CHR' + HgX_2 \rightarrow XSiR_2CH_2CHR'CH_2HgX \xrightarrow{R''OH} \rightarrow R''OSiR_2CH_2CHR'CH_2HgX \rightarrow O(SiR_2CH_2CHR'CH_2HgX)_2.$$

In an alcoholic medium these compounds are apparently formed as a result of heterofunctional condensation catalysed by mercury salts:

$$\equiv SiX + R''OSi{\equiv} \xrightarrow{HgX_2} \equiv Si{-}O{-}Si{\equiv} + R''X.$$

Mercury salts cleave 1,1,3,3-tetramethyl-1,3-disilacyclobutane even more readily (the rate of its cleavage by $HgCl_2$ is four times greater than the rate of cleavage of 1,1-dimethylsilacyclobutane)[165–168]:

$$Me_2Si\begin{matrix}CH_2\\CH_2\end{matrix}SiMe_2 + HgX_2 \rightarrow XSiMe_2CH_2SiMe_2CH_2HgX \xrightarrow{R''OH} \rightarrow R''OSiMe_2CH_2SiMe_2CH_2HgX \rightarrow O[SiMe_2CH_2SiMe_2CH_2HgX]_2.$$

The homogeneous reaction of sila- and 1,3-disila-cyclobutanes with $Hg(NO_3)_2$ in an alcoholic medium proceeds in the same direction as for $HgCl_2$ or $HgAc_2$, but in a heterogeneous medium (when aqueous mercury nitrate solutions are used) oligomeric (telomeric) mercuration products are formed[169,170] probably via the mechanism

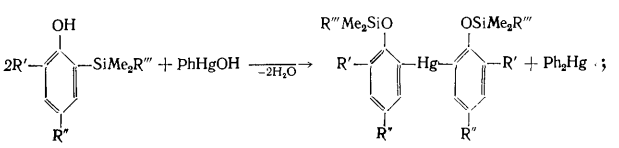
$$R_2Si\begin{matrix}CH_2\\CH_2\end{matrix}R' + Hg(NO_3)_2 \xrightarrow{H_2O} [O_3NSiR_2CH_2R'CH_2HgNO_3] \xrightarrow{nR_2Si\diamondsuit R'} \rightarrow \{O_3N[SiR_2CH_2R'CH_2]_{n+1}HgNO_3\} \xrightarrow{H_2O} HO[SiR_2CH_2R'CH_2]_{n+1}HgNO_3 \rightarrow O\{[SiR_2CH_2R'CH_2]_{n+1}HgNO_3\}_2;$$
$$R = Me, \text{ or Ph}; R' = CH_2, \text{ or } SiR_2.$$

Evidently in this case the primary cleavage product, containing the labile Si–O–NO_2 group, is itself capable of breaking the sila- or 1,3-disila-cyclobutane ring, which leads to the formation of oligomeric compounds.

Five-membered heterocycles with one or two silicon atoms in the ring do not react with mercury salts[167]. It has been suggested that the rate of these reactions is controlled by the electrophilic attack by the HgX^+ cation.

(d) Mercuration of aromatic organosilicon derivatives. The reactions of mercury salts with organosilicon compounds in which the silicon atom is linked directly to an aromatic ring lead in all cases to the dissociation of the Si–Ar bond and not to the mercuration of the ring[171–176].

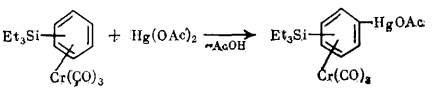
Sterically hindered *o*-trialkylsilylphenols react with PhHgOH or Ph_2Hg, forming the corresponding bis-(2-trialkylsiloxyphenyl)mercuranes[177–180]:



$R' = R'' = CMe_3$, $R''' = Me$; $R' = SiMe_3$, $R'' = CMe_3$, $R''' = Me$; $R' = CMe_3$, $R'' = SiMe_3$, $R''' = Me$; $R' = R'' = CMe_3$, $R''' = Ph$.

When PhHgOH interacts with *o*-trialkylsilylphenols containing a less hindered OH group, polymeric arylmercury oxides which do not contain silicon are formed[178]. If the trialkylsilyl group is in the *para*-position relative to the hydroxy-groups, mercuration does not occur[181] and oxidation of the organosilicon phenols is observed.

The interaction of triethylsilylbenzenechromium tricarbonyl by mercury acetate in glacial acetic acid leads to mercuration in the aromatic ring without the elimination of the triethylsilyl group [182]:



The separation of the silicon atom from the aromatic ring by the $-(CH_2)_nO$-group permits the smooth mercuration of the ring [183]:

$$X_3Si(CH_2)_nOC_6H_4Y + Hg(OAc)_2 \xrightarrow{-AcOH} X_3Si(CH_2)_nOC_6H_3Y(HgOCOCH_3);$$

X = Me, MeO, or EtO;

Y = H, OMe-*o*, Me-*p*; $n = 1, 3$.

Using an excess of mercury acetate, it is possible to convert compounds of the type $X_3Si(CH_2)_nOPh$ into [bis(acetoxymercuri)phenoxyalkyl]trialkyl- or [bis(acetoxymercuri)phenoxyalkyl]trialkoxy-silanes $X_3Si(CH_2)_nOC_6H_3 \cdot (HgOAc)_2$. [183]

2. Properties

Organomercury compounds containing the $Si-(-C-)_n-Hg$ group are fairly resistant to the action of atmospheric oxygen, moisture, and light, in contrast to compounds with the Si–Hg bond. They also exhibit a comparatively high thermal stability. Thus many compounds of the type R_3SiCH_2HgR' can be distilled *in vacuo* without appreciable decomposition and can be successfully separated by the gas–liquid chromatography (GLC) [139]. Bis(trimethylsilylmethyl)mercury decomposes slowly only at 200°C (to the extent of 5% after 100 h) [145], forming mercury, tetramethylsilane, and $Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$.

However, in the photolysis of $(Me_3SiCH_2)_2Hg$ vigorous decomposition is observed with formation of mercury, methane, tetramethylsilane, and small amounts of $Me_3SiCH_2HgCH_2SiMe_2CH_2CH_2SiMe_3$, $Me_3SiSiMe_3$, $(Me_3SiSiMe_2)_2$, and $(Me_3SiCH_2CH_2SiMe_2CH_2)_2$. [145] When bis[tris(trimethylsilyl)methyl]mercury is acted upon by light, the relatively stable free radicals $[(CH_3)_3Si]_3Si^{\cdot}$ are generated [184]. They are only slightly less stable than $(Ph_3C^{\cdot})$:

$$[(Me_3Si)_3C]_2Hg \rightarrow 2(Me_3Si)_3C^{\cdot} + Hg .$$

The products of the mercuration of Si-substituted alkenylsilanes and organosilicon derivatives of mercury, formed when sila- or 1,3-disila-cyclobutanes are cleaved by mercury salts, exhibit an inadequate thermal stability. They do not distill *in vacuo*, since they readily eliminate metallic mercury.

Treatment of organosilicon derivatives of mercury of the type $Me_3SiCH(HgOAc)CH_2OH$ with saturated solutions of alkali metal halides leads to the exchange of the acetoxy-group at the mercury atom for the halogen [154]:

$$Me_3SiCH(HgOAc)CH_2OH + MX \rightarrow Me_3SiCH(HgX)CH_2OH + MOAc;$$

M = K or Na; X = Cl, Br, or I.

The amorphous halogenomercuri-derivatives formed under these conditions exchange the HgX group for the halogen in reactions with the latter [154,156]:

$$Me_3SiCH(HgX)CH_2OH + X_2 \rightarrow Me_3SiCHXCH_2OH + HgX_2 .$$

The reactions of $Me_3SiC{\equiv}CHgOAc$ and $Me_3SiC{\equiv}CHgI$ with iodine lead to the formation of trimethyliodoethynylsilane [162]:

$$(CH_3)_3SiC{\equiv}CHgX + I_2 \rightarrow (CH_3)_3SiC{\equiv}CI + IHgX;$$

X = OAc or I.

[(Phenyldimethylsilyl)methyl]mercury bromide is converted into the corresponding mercury acetate when acted upon by silver acetate [143]; the mercury acetate readily symmetrises under the influence of a 0.02 M perchloric acid solution:

$$PhMe_2SiCH_2HgBr \xrightarrow[-AgBr]{AgOAc} PhMe_2SiCH_2HgOAc \xrightarrow{HClO_4} (PhMe_2SiCH_2)_2Hg + Hg(OAc)_2$$

When acted upon by a saturated solution of hydrogen chloride in ethanol, compounds of the type Me_3SiCH_2HgR are cleaved [138] via the mechanism

$$Me_3SiCH_2HgR + HCl \xrightarrow{C_2H_5OH} \begin{cases} \rightarrow Me_4Si + RHgCl \ (R = Me \text{ or } n\text{-}C_6H_{13}) \\ \rightarrow Me_3SiCH_2HgCl + RH \ (R = Ph) \end{cases}.$$

This reaction made it possible to estimate the relative electronegativities of the substituent R linked to the mercury atom, which decrease in the following sequence:

$$Ph > Me_3GeCH_2 > Me_3SiCH_2 > Me > n\text{-}C_6H_{13} > Me_3CCH_2.$$

The higher electronegativity of the Me_3GeCH_2 group compared with that of the Me_3SiCH_2 group is indicated by the reaction [147]

$$2Me_3SiCH_2HgCH_2GeMe_3 + HCl \rightarrow \underset{(80\%)}{Me_4Ge} + \underset{(85\%)}{Me_3SiCH_2HgCl} + \underset{(20\%)}{Me_4Si} + Me_3GeCH_2HgCl .$$

However, all these data concerning the relative ease of elimination of substituents from the mercury atom characterise not only their electronegativity, but also their steric effect. For example, although the $Me_3SiSiMe_2$ group has stronger electron-donating properties than the Me_3Si group, it is eliminated from the mercury atom by hydrogen chloride with greater difficulty owing to steric hindrance [139]. The more bulky $Me_3CSiMe_2CH_2$ and $(Me_3Si)_2CH$ group are also split off from the mercury atom with greater difficulty than the Me_3SiCH_2 group.

Compounds of the type Me_3SiCH_2HgR' are also cleaved by mercury(II) chloride [138]:

$$Me_3SiCH_2HgC_6H_{13} + HgCl_2 \rightarrow Me_3SiCH_2HgCl + C_6H_{13}HgCl .$$

Bis(triorganylsilylmethyl)mercuranes interact with alkali metals, splitting off mercury and forming the corresponding alkali metal derivatives [140–142,185]:

$$(R_3SiCH_2)_2Hg + 2M \rightarrow 2R_3SiCH_2M + Hg ,$$

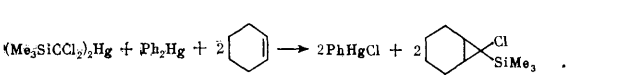
where M = Li, Na, K, Rb, or Cs.

This reaction constitutes a convenient method for the synthesis of organosilicon derivatives of alkali metals.

Tris(trimethylsilylmethyl)aluminium has been obtained similarly [186]:

$$3(Me_3SiCH_2)_2Hg + 2Al \rightarrow 2(Me_3SiCH_2)_3Al + 3Hg .$$

On heating, compounds of the type $(Me_3SiCX_2)_2Hg$ ($X_2 = Cl_2$, HBr, ClBr, or Br_2) give rise to the carbenes Me_3SiCH, Me_3SiCCl, and Me_3SiCBr, [150–152] which are capable of adding to the double bonds of unsaturated compounds:



In view of the high stability of compounds containing the $Si-(-C-)_n-Hg$ group, in contrast to compounds with the Si–Hg bond, the former can find practical applications. Thus compounds having the general formula $ROCOHgCH_2C \cdot (OR')YA_nSi(R'')_a(X)_b$ ($R = R' = R'' =$ alkyl; Y = H or Me; A = alkylene; X = alkoxy- or acetoxy-group; $a = 0-2$; $b = 3-a$) can serve as fungicidal additives to silicone elastomers [161].

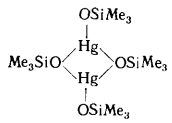
IV. COMPOUNDS CONTAINING THE Si–X–Hg (X = O, S, Se, Te, OR N) GROUP

1. Compounds Containing the Si–O–Hg Group

One of the most widely used methods for the synthesis of compounds containing the Si–O–Hg group involves the reaction of alkali metal triorganylsilanoxides with mercury salts. Mercury(II) chloride reacts with sodium trimethylsilanoxide in dioxan, forming the ether-soluble bis(trimethylsiloxy)mercury, which is extremely sensitive to moisture [187]:

$$2Me_3SiONa \xrightarrow[-2NaCl]{HgCl_2} (Me_3SiO)_2Hg \xrightarrow[-HgO]{H_2O} 2Me_3SiOH \ .$$

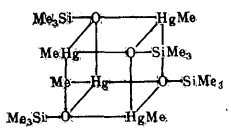
This compound sublimes in a high vacuum at 90°C, forming crystals. Determination of the molecular weight revealed its dimeric structure [188]:



At approximately 0°C bis(trimethylsiloxy)mercury slowly decomposes with dissociation of the Si–C bond:

$$(Me_3SiO)_2Hg \rightarrow Me_3SiOHgMe + 1/n\,(Me_2SiO)_n \ .$$

Methyl(trimethylsiloxy)mercury, obtained by treating Me_3SiONa with methylmercury chloride, is more stable and is readily soluble in organic solvents [188–190]. It is associated and has a tetrameric structure in the crystalline state [190,191]:



When $HgCl_2$ interacts with sodium triphenylsilanoxide (in molar proportions of 1 : 2) in ether, sodium chloride precipitates instantaneously and bis(triphenylsiloxy)mercury is formed [192]. However, even when the solvent is removed *in vacuo* (< 20°C), the decomposition of this compound begins. This results in a 34% yield of phenyl(triphenylsiloxy)mercury and a solid polymer which melts in the range 135–250°C:

$$2Ph_3SiONa + HgCl_2 \xrightarrow[-2NaCl]{} [Ph_3SiO]_2Hg \rightarrow Ph_3SiOHgPh + Ph_3SiO\,(Ph_2SiO)_n\,HgPh \ .$$

When the proportions of $HgCl_2$ and PhSiONa are 1 : 1, a similar polymer and PhHgCl are formed, which indicates an analogous process (with dissociation of the Si–C bond):

$$R_3SiONa + HgCl_2 \rightarrow R_3SiO\,(R_2SiO)_n\,HgCl + RHgCl \ .$$

Phenyl(triphenylsiloxy)mercury can be obtained also by another procedure [192]:

$$Ph_3SiOK + PhHgCl \rightarrow Ph_3SiOHgPh + KCl \ .$$

This compound is not hydrolysed by water but is cleaved on treatment with HCl, forming triphenylsilanol and PhHgCl. It is stable at room temperature, but above the melting point decomposes with formation of Ph_2Hg and $Ph_3SiO(Ph_2SiO)_nHgPh$.

Organosilicon derivatives of mercury containing the Si–O–Hg group can be obtained [193] by the reaction of RHgX (R is an organic group and X the hydroxy-group or the residue of an inorganic or acetic acid) with silicon tetrachloride, tetraethoxysilane, metal silicates, and silicic acid. After prolonged refluxing of a mixture of $SiCl_4$ and mercury(II) oxide in a polar solvent (acetonitrile, nitromethane, etc.) in the presence of mercury(II) chloride [194], perchloro-oligosiloxanes $Cl_3Si(OSiCl_2)_nCl$ (n = 1–4), boiling in the range from 190° to 262°C at 15 mmHg, and a solid having the composition $ClHgOSiCl_3$ are formed.

The attempt to obtain polyphenylmercurosiloxanes by the reaction of disodium diphenylsilanedioxide with mercury(II) chloride led only to the formation [195] of octaphenylcyclotetrasiloxane $Ph_2SiOPh_2SiOPh_2SiOPh_2SiO$, but the reaction of diphenylsilanediol with diethylmercury nevertheless made it possible to synthesise the polymeric organosilicon derivative of mercury containing the Si–O–Hg group [195].

The 885 cm^{-1} [192] and 932 cm^{-1} [188] bands in the infrared spectra of triorganylsiloxymercuranes have been assigned to the vibrations of the Si–O–Hg group [188].

2. Compounds Containing the Si–X–Hg Groups (X = chalcogen).

As stated in Section II. 3 (see Table), organosilicon derivatives of mercury containing the Si–X–Hg group are formed when bis(trialkylsilyl)mercuranes interact with sulphur or selenium [50,100,121–123]:

$$(R_3Si)_2Hg + 1/8\,X_8 \rightarrow R_3SiXHgSiR_3 \ ;$$
$$R = Et \text{ or iso-Pr};\ X = S \text{ or Se}.$$

Selective heterolytic cleavage of bis(triethylgermyl)-mercury with triethylsilaneselanol or triethylsilanetellurol leads to the corresponding germanium derivatives [100,196,197]. When the reactants are in proportions of 1 : 2, $(R_3SiX)_2Hg$ is formed together with triethylgermane:

$$(R_3Ge)_2Hg + HXSiR_3 \rightarrow R_3GeHgXSiR_3 + R_3GeH \ ,$$
$$(R_3Ge)_2Hg + 2HXSiR_3 \rightarrow 2R_3GeH + Hg\,(XSiR_3)_2 \ ,$$
$$R = Et;\ X = Se \text{ or Te} \ .$$

Asymmetric compounds containing the Si–X–Hg group readily decompose at room temperature via the mechanism [196,197]

$$R_3GeHgXSiR_3 \rightarrow R_3GeXSiR_3 + Hg \ .$$

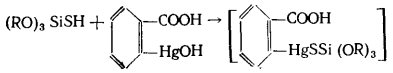
On the other hand, the symmetrical derivatives $(R_3SiX)_2Hg$ have a fairly high thermal stability and do not fully decompose in solution even under prolonged heating (7 h, 130°C). Their decomposition products are the mercury chalcogenide and $(R_3Si)_2X$:

$$(R_3SiX)_2Hg \rightarrow (R_3Si)_2X + HgX \ .$$

Trialkoxysilylthiomercuranes, which are relatively soluble in ether and tetrahydrofuran and are stable in the absence of moisture, have been obtained by the interaction of trialkoxysilanethiols with ethylmercury bromide [198]:

$$(RO)_3SiSH' + EtHgBr \rightarrow (RO)_3SiSHgBr + C_2H_6 \ ;$$
$$R = \text{iso-Pr, } Me_3C, \text{ or } (CH_3)_2CHCH_2CH_2 \ .$$

The formation of a compound containing the Si–S–Hg group is observed in the reaction of trialkoxysilanethiols with *o*-hydroxymercuribenzoic acid. However, the product has not been isolated in a free form [199]:



3. Compounds Containing the Si–N–Hg Group

The exothermic reaction of sodium bis(trimethylsilyl)-amide with mercury(II) bromide in ether yielded di[bis(trimethylsilyl)amino]mercurane [153,200,201]:

$$2\,(Me_3Si)_2NNa + HgBr_2 \rightarrow [(Me_3Si)_2N]_2Hg + 2NaBr\ .$$

The reaction product is a colourless crystalline substance, which distills *in vacuo*, does not form adducts with pyridine or tetrahydrofuran, and is readily hydrolysed to $Hg(OH)_2$ and hexamethyldisilazane.

The force constant, indicating that the Hg–N bond is covalent and single, has been calculated from infrared and Raman spectroscopic data [200]. The Hg–N interatomic distance is 2.23 Å. The band at 406 cm^{-1} in the infrared spectrum was assumed to correspond to the $\nu_{as}(N–Hg–N)$ frequency. The 390 cm^{-1} line in the Raman spectrum corresponds to the $\nu_S(N–Hg–N)$ vibration.

Lithium tris(trimethylsilyl)hydrazide reacts exothermically with mercury(II) chloride or bromide in pentane [202], forming the lithium halide and mercury tris(trimethylsilyl)-hydrazide:

$$2\,(R_3Si)_2N–N(Li)–SiR_3 + HgX_2 \rightarrow 2LiX + (R_3Si)_2N–N\begin{matrix}SiR_3\\ \diagdown\\ Hg–N–N–(SiR_3)_2\\ \diagup\\ SiR_3\end{matrix}\ ;$$

$$R = Me,\ X = Cl\ or\ Br\ .$$

This hydrazide is a crystalline substance, which is readily soluble in petroleum ether, benzene, and THF and is sensitive to moisture. According to cryoscopic data, the compound is monomeric. Its infrared spectrum exhibits the intense asymmetric vibration of the N–Hg–N group with $\nu_{as} = 379\ cm^{-1}$ in the region of low frequencies. The ^1H NMR spectrum is a doublet ($\nu = 0.28,\ 0.26$). [202]

The interaction of lithium bis(trimethylsilyl)amide with alkylmercury halides gave *N*,*N'*-bis(trimethylsilyl)alkylmercuramines in yields up to 85% [203]:

$$(Me_3Si)_2NLi + RHgX \rightarrow (Me_3Si)_2NHgR + LiX\ ;$$

$$R = Me\ or\ Et;\quad X = Cl\ or\ Br\ .$$

They are colourless liquids which distill *in vacuo*. ^1H NMR spectra: $\delta(CH_3Hg) = 0.37$ p.p.m., $\delta(CH_3Si) = 0.17$ p.p.m., and $J(^{199}Hg–CH_3) = 157$ Hz were obtained for $CH_3HgN[Si(CH_3)_3]_2$; $\delta(CH_3CHg) = 1.07$ p.p.m., $\delta(CCH_2Hg) = 1.17$ p.p.m., $\delta(SiCH_3) = 0.19$ p.p.m., $J(^{199}Hg–CH_2) = 160$ Hz, and $J(^{199}Mg–CCH_3) = 195$ Hz were found for $C_2H_5HgN.[Si(CH_3)_3]_2$.

Alkyl-*N*,*N'*-bis(triorganylsilyl)mercuramines are useful reagents in the synthesis of many organomercury compounds which are otherwise difficult to obtain. Thus the interaction of $MeHgN(SiMe_3)_2$ with an equimolar amount of water in ether leads to the formation of dimethyldimercury oxide and hexamethyldisilazane in quantitative yields [203]:

$$2\,(Me_3Si)_2NHgMe + H_2O \rightarrow 2\,(Me_3Si)_2NH + MeHgOHgMe\ .$$

The reaction with HN_3 gives rise to mercury azides [203]:

$$(Me_3Si)_2NHgR + HN_3 \rightarrow (Me_3Si)_2NH + RHgN_3\ ;$$

$$R = Me\ or\ Et.$$

The reaction

$$2\,(Me_3Si)_2NHgR + H_2NCN \rightarrow 2\,(Me_3Si)_2NH + (RHg)_2NCN\ ;$$

$$R = Me\ or\ Et.$$

has been used to synthesise bis(organylmercuri)cyanamide. The interaction of *N*,*N'*-bis(trimethylsilyl)methylmercuramine with $HN=P(NMe_2)_3$ yielded tris(dimethylamino)-*N*-(methylmercuri)phosphinimide [204]:

$$(Me_3Si)_2NHgMe + HN=P(NMe_2)_3 \rightarrow (Me_3Si)_2NH + MeHgN=P(NMe_2)_3\ .$$

The reaction with nitroalkanes gives rise to organomercury derivatives of nitronic acids [205]:

$$(Me_3Si)_2NHgR + R'R''CHNO_2 \rightarrow (Me_3Si)_2NH + RHgO\overset{O}{\overset{\|}{N}}=CR'R''\ ;$$

$$R = Me\ or\ Et;\quad R',\ R'' = H\ or\ CH_3.$$

The reaction of $RHgN(SiMe_3)_2$ with diazoacetone or diazoacetophenone is used to synthesise organylmercuridiazoketones and mercuribis(diazoketones) [206]:

$$(Me_3Si)_2NHgR + HC(N_2)COR' \rightarrow (Me_3Si)_2NH + RHgC(N_2)COR'\ ,$$

$$(Me_3Si)_2NHgR + 2HC(N_2)COR' \rightarrow (Me_3Si)_2NH + Hg[C(N_2)COR']_2 + RH\ ;$$

$$R = Me\ or\ Et;\quad R' = Me\ or\ Ph.$$

$[(Me_3Si)_2N]_2Hg$ reacts analogously with 1,3-diketones [201,207,208]:

$$[(Me_3Si)_2N]_2Hg + 2HOCR=CHCOR \rightarrow (Me_3Si)_2NH + Hg(OCR=CHCOR)_2\ ;$$

$$R = Me\ or\ CMe_3.$$

Organyl-*N*,*N'*-bis(trimethylsilyl)mercuramines react with cyclopentadiene to form organylmercuricyclopentadienes [203]:

$$(Me_3Si)_2NHgR + HC_5H_5 \rightarrow (Me_3Si)_2NH + RHgC_5H_5\ ;$$

$$R = Me\ or\ Et\ .$$

Bis(cyclopentadienyl)mercury is formed similarly from $Hg[N(SiMe_3)_2]_2$ [209]:

$$[(Me_3Si)_2N]_2Hg + 2HC_5H_5 \rightarrow 2\,(Me_3Si)_2NH + Hg(C_5H_5)_2\ .$$

Mercury derivatives of tris(pentafluorophenyl)silane and tris(pentafluorophenyl)germane [21,32,210] as well as triphenylstannane [211] have been obtained with the aid of di[bis(trimethylsilyl)amino]mercury [211]:

$$[(Me_3Si)_2N]_2Hg + 2H\Theta(C_6F_5)_3 \rightarrow 2\,(Me_3Si)_2NH + Hg[\Theta(C_6F_5)_3]_2\ ;$$

$$\Theta = Si\ or\ Ge.$$

$$[(Me_3Si)_2N]_2Hg + 2HSnPh_3 \rightarrow 2\,(Me_3Si)_2NH + Hg(SnPh_3)_2\ .$$

The hydrolytic instability of compounds containing the Si–X–Hg group limits their industrial manufacture and practical employment. However, they are extremely useful in the preparative synthesis of organomercury and organosilicon compounds which are otherwise difficult to obtain.

V. COMPOUNDS CONTAINING THE $Si–(–C–)_n–X–Hg$ GROUP

Among compounds of this type, only examples with X = Ge or Sn are known [212,213]. Di[tris(trimethylsilylmethyl)germyl]mercurane has been obtained by treating $(Me_3SiCH_2)_3GeH$ with diethylmercury [213]:

$$2\,(Me_3SiCH_2)_3GeH + Et_2Hg \rightarrow [(Me_3SiCH_2)_3Ge]_2Hg + 2EtH\ .$$

Di[tris(trimethylsilylmethyl)stannyl]mercurane has been synthesised by a similar mechanism [212]:

$$2\,(Me_3SiCH_2)_3SnH + Et_2Hg \rightarrow [(Me_3SiCH_2)_3Sn]_2Hg + 2EtH\ .$$

This compound is one of the products of the exchange reaction of the ester of mercurybisacetic acid with di[tris(trimethylsilylmethyl)stannyl]cadmium [213]:

$$[(Me_3SiCH_2)_3Sn]_2Cd + Hg(CH_3COOMe)_2 \rightarrow [(Me_3SiCH_2)_3Sn]_2Hg + Cd(CH_3COOMe)_2\ .$$

The asymmetric compounds $(Me_3SiCH_2)_3SnHgCH_2COOMe_3$ and $(Me_3SiCH_2)_3SnCdCH_2COOMe$ are then formed as intermediates.

Di[tris(trimethylsilylmethyl)stannyl]mercury exhibits an anomalously high thermal stability compared with its analogues $(R_3Sn)_2Hg$, where R = H, alkyl, or phenyl. This can be explained by the stabilising effect of the Me_3SiCH_2 group.

$[(Me_3SiCH_2)_3Sn]_2Hg$ is a crystalline substance which melts without decomposition. Its reactivity does not differ appreciably from that of bis(triethylsilyl)mercury and similar compounds [212,214-216]. Its solutions in hexane and THF are stable at 20°C. Thermal decomposition in the absence of solvents leads to the formation of mercury, tetrakis(trimethylsilylmethyl)stannane, and tin [221,214], probably via the intermediate formation of hexakis(trimethylsilylmethyl)distannane, which then disproportionates via the mechanism

$$2\,[(Me_3SiCH_2)_3Sn]_2 \xrightarrow{150^\circ,\ 10\ h} 3\,(Me_3SiCH_2)_4Sn + Sn\ .$$

Oxidation with atmospheric oxygen in THF leads to the formation of mercury and hexakis(trimethylsilylmethyl)-distannoxane [218]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + {}^1/_2O_2 \rightarrow [(Me_3SiCH_2)_3Sn]_2O + Hg\ .$$

The exchange reaction with $HgCl_2$ in THF at 20°C is completed after 30 min and leads to the quantitative formation of mercury and $(Me_3SiCH_2)_3SnCl$ [212,214]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + HgCl_2 \rightarrow 2\,(Me_3SiCH_2)_3SnCl + 2Hg\ .$$

The interaction of di[tris(trimethylsilylmethyl)stannyl]-mercury with $Hg[C(CF_3)_3]_2$ leads to the formation of an asymmetric stannylmercury compound, which is demercurated with simultaneous β-decomposition [95,214]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + Hg[C(CF_3)_3]_2 \rightarrow 2\,(Me_3SiCH_2)_3SnHgC(CF_3)_3 \rightarrow$$
$$\rightarrow 2\,(Me_3SiCH_2)_3SnF + 2Hg + 2\,(CF_3)_3C{=}CF_2\ .$$

Elemental iodine readily cleaves the Sn–Hg bond [213]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + 2I_2 \rightarrow 2\,(Me_3SiCH_2)_3SnI + HgI_2\ .$$

Metallic lithium exchanges with mercury to form the corresponding stannyl-lithium derivative [213,217]:

$$[(Me_3SiCH_2)_3Sn]_2Hg + 2Li \rightarrow 2\,(Me_3SiCH_2)_3SnLi + Hg\ .$$

However, when the reaction is carried out in benzene, the main product is hexakis(trimethylsilylphenyl)distannane.

VI. COMPLEXES OF ORGANOSILICON COMPOUNDS WITH MERCURY SALTS

Triorganylsilylmethyl derivatives of phosphorus and arsenic form stable complexes with mercury halides. Thus tris(trimethylsilylmethyl)phosphine and tris(trimethylsilylmethyl)arsine react with mercury(II) chloride to form crystalline adducts [218,219]:

$$(Me_3SiCH_2)_3E + HgCl_2 \rightarrow (Me_3SiCH_2)_3E \cdot HgCl_2$$
$$E = P \text{ or } As.$$

When a solution of methyltris(trimethylsilylmethyl)arsonium iodide is refluxed with mercury(II) iodide in ethanol, methyltris(trimethylsilylmethyl)arsonium iodomercurate is formed [218]:

$$(Me_3SiCH_2)_3AsMeI + HgI_2 \rightarrow [(Me_3SiCH_2)_3AsMe]\,HgI_3\ .$$

The complexes of diphenyl-(*p*-triethylsilylphenyl)arsine with mercury(II) halides [*p*-$(Et_3Si)C_6H_4AsPh_2.HgCl_2$, *p*-$(Et_3Si)C_6H_4AsPh_2.HgBr_2$, and *p*-$(Et_3Si)C_6H_4AsPh_2.HgI_2$] are soluble in benzene and have distinct melting points (188°, 181°, and 139.5°C respectively), so that they can be used for the identification of triorganyl-silylphenylarsines [220].

The interaction of mercury(II) bromide with $[Ph_3PCH_2.SiMe_3]^+Br^-$ in methanol led to a water-soluble phosphonium complex having the composition $[Ph_3PCH_2SiMe_3]^+\,HgBr_3^-$. [221]

The reactions of mercury(II) chloride and methylmercury chloride with $Me_3P{=}CHSiMe_3$ or $Me_3P{=}C(SiMe_3)_2$ lead to the formation of mercurated silylphosphonium salts [153,164] $Me_3P{=}CHSiMe_3.HgCl_2$. When the reactant ratio is 2 : 1, the products are

$$\left[\begin{matrix} Me_3PCHHgCHPMe_3 \\ | \qquad\quad | \\ Me_3Si \qquad SiMe_3 \end{matrix}\right]^{2+} 2X^-,\ X = Cl \text{ or } Br\ .$$

In the reaction of bis(tricarbonylnitrosyliron)mercury with tris(trimethylsilylmethyl)phosphine one of the CO groups is substituted quantitatively [222]:

$$2\,(Me_3SiCH_2)_3P + Hg[Fe(CO)_3(NO)]_2 \xrightarrow[-CO]{} Hg[Fe(CO)_2(NO)P(CH_2SiMe_3)_3]_2\ .$$

On interaction with the same phosphine, bis(tetracarbonylcobalt)mercury forms a complex which undergoes an exchange or disproportionation reaction in the presence of mercury(II) halides [222]:

$$2\,(Me_3SiCH_2)_3P + Hg[Co(CO)_4]_2 \xrightarrow[-CO]{} [(Me_3SiCH_2)_3PCo(CO)_3]_2Hg \xrightarrow{+HgX_2}$$
$$\rightarrow 2\,(Me_3SiCH_2)_3PCo(CO)_3HgX\ .$$

Trialkylsilylmethanethiols react with mercury(II) chloride to form stable crystalline adducts [223]:

$$R_3SiCH_2SH + HgCl_2 \rightarrow [(R_3SiCH_2SH)_2Hg]Cl_2\ .$$

Bis(trimethylsilylmethyl) sulphide reacts with mercury(II) iodide to form $(Me_3SiCH_2)_2S.HgI_2$. [223] Compounds having the general formula $[XC_6H_4Hg]_2SiF_6$, where X = H or a halogen, are obtained by treating a phenylmercury salt with fluorosilic acid [224].

All the facts described above show that further studies in the field of organosilicon derivatives of mercury will prove extremely useful for the development of theoretical and particularly synthetic organic and organoelemental chemistry. There is also no doubt that, apart from the applications already described, new fields of the practical use of these compounds will be discovered.

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Molecular Weight Distribution in the Production of Homopolymers

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The principal mathematical methods for the simulation of the molecular weight distributions (MWD) in homopolymers obtained by radical polymerisation are examined. An attempt is made at a survey and a systematic arrangement of mathematical models in terms of kinetic mechanisms, type of reaction apparatus, and the mathematical procedure used.
The bibliography includes 45 references.

CONTENTS

I. Introduction 979
II. Classical method for the calculation of the molecular weight distribution 980
III. Method of generating functions 983
IV. The continuous variable method 984
V. Polymerisation at high conversions 985
VI. Calculation of the molecular weight distribution in the production of homopolymers in a cascade of reactors 987

I. INTRODUCTION

In studies on polymerisation processes and the properties of polymers much attention is devoted to the investigation of the distribution of polymer and radical chains with respect to molecular weight. Information about the characteristics of the molecular weight distribution (MWD) is necessary for many theoretical and practical problems in polymer chemistry. Nowadays there is an appreciable need to employ MWD in the technology of polymers. The modern principles of the strategy for the simulation of large chemical engineering plants, whereby the process can be optimised from a particular point of view, are of interest also for the technology of polymeric materials. This strategy can be applied to the analytical planning of new large-scale polymerisation processes, their optimisation, and the intensification of the existing processes, but an obligatory condition is always the knowledge of MWD. The initial information required for the solution of problems of this class in relation to polymerisation processes includes, apart from the traditional (for chemistry) mathematical description of the technological process and the set of optimisation criteria, a library of mathematical MWD models. The solution of optimisation problems in the field of industrial polymerisation without the calculation of MWD is impossible, since any optimisation of the polymerisation process must assist the solution of the main problem of polymer chemistry—the synthesis of polymeric materials with specified properties, i.e. ultimately materials having the required set of MWD characteristics.

In the study of a polymerisation process technologists have at their disposal a set of models of various types of reaction apparatus in which polymerisation takes place. In selecting the optimisation factor, the specific features of processes of this kind (the set of requirements which the process must meet is described by several factors and it is important that all such factors be optimised simultaneously) are reflected in the application of multifactor optimisation methods. As regards the use of mathematical MWD models, there is no such clarity. This review is an attempt at a survey and systematic account of mathematical MWD models with respect to the specific mechanism, type of reaction apparatus, and the mathematical procedures employed. The proposed ordered arrangement of the multiplicity of methods for the calculation of distribution functions is designed for a broad class of studies on polymerisation processes with the aim of a rational control of these processes. A systematic arrangement of MWD models is considered in relation to homopolymers obtained in radical polymerisation, although the proposed approach can be used also for branched polymers by extending the set of mathematical methods, for example, by including the method of the theory of graphs developed in topology and introduced for the first time in studies on the chemical kinetics of multistage branched enzymatic catalytic reactions[1-3]. However, the aim of the present review was restricted to the consideration of the MWD in the formation of linear homopolymers by a free radical mechanism.

Table 1. Kinetic scheme for radical polymerisation.

Designation	Reaction mechanism	Reaction rate equation
Initiation		
decompn. of initiator	$I \xrightarrow{k_i} 2R_c$	
start of reaction	$R_c + M \rightarrow R_1$	$w_i = f(I)$
Chain propagation	$R_r + M \xrightarrow{k_p} R_{r+1}$	$w_p = k_p M R_r$
Chain transfer:		
via the monomer	$R_r + M \xrightarrow{k_f} P_r + M^{\cdot}$	$w_f = k_f M R_r$
via the solvent	$R_r + S \xrightarrow{k_{fs}} P_r + S^{\cdot}$	$w_{fs} = k_{fs} S R_r$
Chain termination:		
by recombination	$R_r + R_s \xrightarrow{k_{t_1}} P_{r+s}$	$w_{t_1} = k_{t_1} R_s R_r$
by disproportionation	$R_r + R_s \xrightarrow{k_{t_2}} P_r + P_s$	$w_{t_2} = k_{t_2} R_s R_r$
via the monomer	$R_r + M \xrightarrow{k_{t_3}} P_{r+1}$	$w_{t_3} = k_{t_3} M R_r$
spontaneous	$R_r \xrightarrow{k_{t_4}} P_r$	$w_{t_4} = k_{t_4} R_r$

The generally accepted kinetic mechanism of a free-radical polymerisation process, which includes elementary chain initiation, chain transfer, and chain termination reactions, is presented in Table 1, where the following notation is used: R_C is the primary radical formed on decomposition of the initiator I, R_r and P_r are respectively

the polymer radical and an inactive polymer molecule consisting of r monomer units, M is the monomer molecule, S the solvent molecule, M$^{\cdot}$ and S$^{\cdot}$ are the corresponding low-molecular-weight radicals, w_i and w_p are the rates of chain initiation and propagation, w_f and w_{fs} the rates of chain transfer via the monomer and the solvent, w_{t_1}, w_{t_2}, w_{t_3}, and w_{t_4} the rates of chain termination via recombination, disproportionation, via the monomer, and via a spontaneous mechanism respectively, and k_p, k_f, and k_t the rate constants for the corresponding reactions. In the equations presented for the rates of the elementary reactions and throughout the review, M, R_r, S, and P_r denote the concentrations of the corresponding substances.

Apart from the kinetic mechanism of the polymerisation process and the rates of the elementary reactions determined by it, the characteristics of the MWD of the polymer formed are influenced by the mass-exchange conditions during the reaction, which depend mainly on the type of reaction apparatus used. In the present review we shall consider the following extreme idealisations: continuous operation ideal displacement reactor, periodic-operation mixing reactor, and ideal continuous-operation mixing reactor. The hydrodynamic conditions for reactors of the intermediate type permit their description with the aid of combined models, including as their elements the above idealised reactor types. Evidently in systems of the first type (ideal displacement reactor, periodic-operation mixing reactor) the concentration of the reactants and the characteristics of the MWD are non-stationary (with respect to time for the mixing reactor and with respect to length for the ideal displacement reactor) are satisfactorily described by differential equations in terms of the usual derivatives. In reaction systems of the second type (continuous operation ideal mixing reactor or a cascade of such reactors) the concentration of the reactants and all the MWD characteristics remain constant in time and are described by algebraic equations.

There exist different mathematical approaches whereby analytical MWD models can be obtained. The choice of the method of calculation of the distribution with respect to molecular weights is determined by the kinetic mechanism and, to a greater extent, by the simplifying assumptions adopted concerning the polymerisation kinetics. Frequently the abandonment of one hypothesis entails the necessity to employ a new mathematical procedure. The methods for the calculation of the MWD considered in the present review have a kinetic bias in the simulation of the molecular weight distributions of polymers, which is based on the physical chemistry of the process. The statistical approach to the calculation of the MWD, based on the estimation of the probability of the summation of polymer chains of the given size without an explicit allowance for the process kinetics, described in a number of monographs[4-6], is not considered in this review. The statistical approach is known to be phenomenological in character overall. With the aid of the statistical distribution, it is possible to characterise rapidly the polymerisation mechanism in broad outline and to predict the approximate MWD parameters of the polymer obtained under specified conditions. Furthermore, in the calculation of the MWD at the end of an industrial technological process, organised with the aid of reactors of different types, it is necessary to know the law governing the evolution of this distribution in time in addition to the adoption of a statistical distribution as a set of exponential functions of the same type. On the other hand, in the kinetic approach account is taken not only of the kinetic mechanism of the polymerisation process but also of the way in which the reaction is carried out (the type of reaction apparatus). The physics and chemistry of the process are reflected in the final distribution, which establishes a relation between the MWD and the parameters of the polymerisation process and this makes it possible to regulate the MWD.

II. CLASSICAL METHOD FOR THE CALCULATION OF THE MOLECULAR WEIGHT DISTRIBUTION

The analytical method for the calculation of the MWD in polymers, which can now be properly referred to as classical since it was used in early studies on the calculation of the MWD, [6-9,11] consists of a direct solution of a system of an infinite number of material balance equations for all the components of the polymerisation system.

We shall explain the essential features of this method in relation to the calculation of the MWD in a reaction of the periodic type quoted by Bamford et al.[6]; a radical polymerisation reaction takes place in the reactor via the kinetic mechanism illustrated in Fig. 1, where $k_{t_3} = 0$ and $k_{t_4} = 0$, i.e. chain termination takes place only via recombination and disproportionation. The equations for the rates of change of the concentrations of the active and inactive polymer radicals and the monomer assume the following form in this instance:

$$\frac{dR_1}{dt} = w_i - k_p M R_1 + (k_{fs}S + k_f M)\sum_{i=2}^{\infty} R_i - (k_{fs}S + k_f M)R_1 - (k_{t_1} + k_{t_2})R_1 \sum_{i=2}^{\infty} R_i, \quad (1)$$

$$\frac{dR_r}{dt} = k_p M R_{r-1} - k_p M R_r - (k_{fs}S + k_f M)R_r - (k_{t_1} + k_{t_2})R_r \sum_{i=2}^{\infty} R_i, \quad (2)$$

$$\frac{dM}{dt} = w_i + k_p M \sum_{i=2}^{\infty} R_i + k_f M \sum_{i=2}^{\infty} R_i, \quad (3)$$

$$\frac{dP_r}{dt} = (k_{fs}S + k_f M)R_r + \frac{1}{2}k_{t_1}\sum_{k=1}^{r-1} R_k R_{r-k} + k_{t_2}R_r \sum_{i=2}^{\infty} R_i, \quad (4)$$

$$r = 2, 3, \ldots \infty.$$

Calculation of the MWD from an infinite system of differential equations (1)–(4) without the adoption of any additional simplifications is unduly difficult. The mathematical method for the calculation of the MWD under consideration postulates the use of the following assumptions, normally adopted in the kinetics of radical polymerisation.

Firstly, it is assumed that at low degrees of conversion the rate of formation of radicals becomes at some instant equal to the rate of their disappearance. This assumption makes it possible to set dR_r/dt and dR_1/dt equal to zero which simplifies further mathematical treatment. There exists a criterion of the applicability of the hypothesis of "quasi-stationarity" or the "Bodenstein–Semenov hypothesis": the residence time in the reaction zone τ is incomparably longer than the time required for the polymer radical to attain stationary conditions (τ_{st}). The time τ_{st} agrees fairly accurately with the average lifetime of the polymer radicals[10].

However, in many cases the validity of this hypothesis is doubtful. In the first place caution must be exercised in applying it when one is considering adiabatic polymerisation conditions. It follows from general considerations that, depending on the activation energy for the decomposition of the initiator and the destruction of the radicals, in an adiabatic process an increase of temperature in the system should have different effects on the rates of formation and destruction of macroradicals.

An increase of the temperature of the reaction medium should then have a much greater influence on the rate of decomposition of the initiator because of the much higher activation energy for the initiation reaction. Therefore, over a fairly long reaction temperature range, a case may arise where the application of the hypothesis of quasi-stationary concentrations becomes incorrect. It has been established[13] theoretically that there is an appreciable difference between the quasi-stationary and non-stationary adiabatic polymerisation conditions (Fig. 1). Evidently the application of the Bodenstein–Semenov hypothesis is unjustified also in the case of an extremely low initiator concentration, since the attainment of stationary conditions is then limited by the initiator concentration. However, in the vast majority of cases of isothermal free-radical polymerisation reactions the MWD obtained using the hypotheses of quasi-stationary concentrations and without it agree satisfactorily[8].

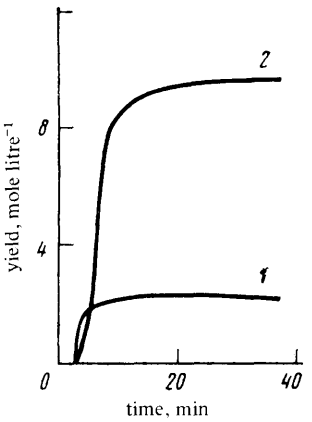


Figure 1. Time variation of the yield of the polymer[13]: 1) with the quasi-stationary hypothesis; 2) without the quasi-stationary hypothesis.

Secondly, the rate constants for the elementary reactions are assumed to be independent of the radical chain length and the degree of conversion of the reaction mixture, which makes it possible to characterise with the aid of a single constant all the steps of elementary reactions of one type. Evidently this assumption greatly simplifies the calculations. However, it has been shown[14] that the hypothesis that the polymerisation reaction rate constants are independent of the length of the macromolecule is in general not justified theoretically and must be proved for each specific case.

Thirdly, it is assumed that, for fairly long chains, the monomer is mainly consumed in the formation of the polymer chain, which makes it possible, by neglecting the consumption of the monomer in initiation and chain transfer, to write instead of Eqn. (3)

$$-\frac{dM}{dt} \cong k_p M \sum_i R_i, \qquad (3')$$

where ΣR_i is the concentration of "living" macromolecules.

Summation of Eqns. (1) and (2), where $r = 2-\infty$, using the hypothesis of quasi-stationary concentrations and the invariance of the rate constants for the elementary reactions, yields the overall concentration of radicals:

$$R = \sum_i R_i = [w_i (k_{t_1} + k_{t_2})]^{1/2}. \qquad (5)$$

On substituting this value of R in Eqns. (1) and (2), we obtain expressions for R_1 and R_r. Integration of the last two equations using the expressions obtained for R_1 and R_r yields the concentration of polymer molecules P_r consisting of r units. Having calculated P_r for various chain lengths r, we obtain the required molecular weight distribution curve. In the general case it is impossible to obtain an analytical expression for P_r by the above procedure. However, in many special cases (in the absence of individual elementary reactions and for constant concentrations of the monomer and other components) it is possible to solve Eqns. (1)–(4) for P_r, i.e. to obtain in an explicit form the equation of the MWD curve.

If the radical polymerisation reaction is carried out in a continuous-operation reaction, the stationary state is described by a system of algebraic equations, each of which represents the material balance with respect to the rth radical, where $r = 1, 2, \ldots$. We shall now explain how the MWD is calculated for a reaction apparatus of this type, following the work of Thiele[9], who considered a kinetic mechanism of radical polymerisation with chain termination via recombination. The material balance equations for the radicals R_1, R_2, R_3, etc. assume the following form in this instance:

$$2k_i f I + k_f M \sum_i R_i = \theta^{-1} R_1 + k_p M R_1 + k_{t_1} R_1 \sum_i R_i, \qquad (1')$$

$$k_p M R_1 = \theta^{-1} R_2 + k_p M R_2 + k_{t_1} R_2 \sum_i R_i + k_f R_2 M, \qquad (2')$$

$$k_p M R_2 = \theta^{-1} R_3 + k_p M R_3 + k_{t_1} R_3 \sum_i R_i + k_f R_3 M, \qquad (2'')$$

where θ is the average residence time of the polymerising system in the reactor $2k_i f I$ the rate of the initiation reaction, and f the efficiency of the initiation. Summation of Eqns. (1'), (2'), ... yields the expression

$$2k_i f I = \theta^{-1} R + k_{t_1} R^2. \qquad (5')$$

We may note that here we are using in essence the assumption that the rate constants for the elementary reactions are independent of chain length. Successive representations of R_r in terms of R_{r-1} yield

$$R_r = \frac{(k_p M)^{r-1} (2k_i f I + k_f M R)}{[\theta^{-1} + (k_p + k_f) M + k_{t_1} R]^r}. \qquad (6)$$

The substitution of the expression for the overall concentrations of macroradicals R from Eqn. (5') in the above formula yields the distribution of active radicals along the chain length. Taking into account Eqn. (6), we obtain the required distribution of polymer chains P_r from the material balance equation for the polymer:

$$\theta^{-1} P_r = \frac{k_{t_1}}{2} \sum_{k=1}^{r-1} R_k R_{r-k} + k_f R_r M. \qquad (7)$$

A considerable mathematical simplification is achieved compared with a periodic-operation reactor, since there is no need to integrate differential equations, which is frequently impossible in terms of quadratures and in the simpler version complex mathematical transformations are needed. This extends the range of models for which it is possible to find an analytical expression of the MWD.

Furthermore, the very expressions for the MWD simplify compared with a periodic-operation reactor as a result of the constancy of the concentrations of all the components of the polymerising system.

If it is assumed that the chain lifetime is short compared with the residence time in the reactor, then evidently the probability that the active radical leaves the reactor before it undergoes chemical reaction and loses its activity is small. This finding is reflected in the initial system of algebraic equations by the relatively low value of the $\theta^{-1}R_r$ terms. The system of algebraic equations for active radicals in a continuous-operation reactor is then identical to the quasi-stationary condition for a periodic-operation reactor and the distributions of radicals with respect to length should be similar for reactors of both types.

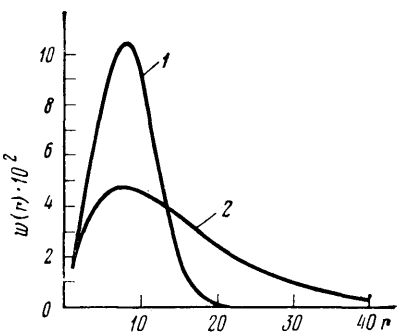


Figure 2. The influence of the type of reactor on the MWD when the lifetime of the active radicals is comparable to the residence time in the reactor[7]: 1) periodic-operation reactor; 2) continuous-operation reactor.

In relation to polystyrene, the lifetime of the growing chain of which is measured in seconds[10,15] while the residence time in the reactor amounts to hours, it has been confirmed[7] that the distribution with respect to the residence time of the species does not affect the MWD of polystyrene. When the residence time of the species in the reaction zone and the chain lifetime are comparable, one must expect a broader MWD for the polymer obtained in a continuous-operation reactor compared with a periodic-operation reactor. This is confirmed by calculations of the MWD [7] (Fig. 2) and can be accounted for by the influence of segregation and micromixing effects on the rate of reaction[16]. Fig. 2 shows a decrease of the homogeneity of the polymer when the process is carried out in a continuous operation reactor compared with a periodic-operation reactor. Analogous results of the calculation of the MWD in the initiated polymerisation of polystyrene, carried out in reactors of both types on the assumption that chain termination takes place as a result of recombination and that there is no chain transfer reaction, have been obtained by Thiele and Hartman[11].

Compared with the large number of theoretical studies on the calculation of the MWD, there are only a few publications presenting the results of the corresponding experimental investigations. In one of the early studies[12] a satisfactory agreement was obtained between experimental and theoretical molecular weight distributions in polystyrene calculated with the aid of the given method. The theoretical MWD curve for suspension polystyrene, obtained in a periodic operation reactor under ideal mixing conditions, has been compared[17] with experimental data. MWD curves have been calculated[18,19] for polystyrene on the assumption that chain termination takes place solely as a result of recombination and that there is chain transfer via the monomer and the solvent. The influence of the solvent concentration was taken into account in the model by a coefficient obtained experimentally[19] as a correction to the rate constant for chain transfer via the monomer. Among a series of experimental results obtained under the conditions of regulated solvent concentration and solution viscosity, best agreement with calculation is observed for low solution viscosities and low solvent concentrations. These results are illustrated in Fig. 3.

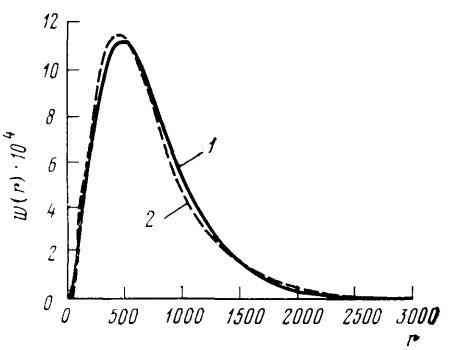


Figure 3. Comparison of the MWD obtained for a low solution viscosity[19]: 1) theoretically; 2) experimentally.

Table 2. Comparison of the calculated and experimental MWD parameters on the basis of the data of Hamielec et al.[19]

MWD parameter	Calculated value	Experimental value
μ_1	48 940	47 460
μ_2	73 920	73 610
μ_2/μ_1	1.51	1.55

The experimental and calculated values of important MWD parameters proved to be very similar under these conditions (Table 2). An experimental characteristic of the MWD (average degree of polymerisation) has been used[17] to determine the elementary reaction constants, which were calculated by minimising the sum of squares of the differences between the measured and calculated average degrees of polymerisation and conversion of styrene.

III. METHOD OF GENERATING FUNCTIONS

The method of generating functions from the theory of random functions has been used in the mathematical simulation of radical polymerisation processes. Liu and Amundson[20] were the first to introduce the above method in the study of processes of this kind. In the investigation of discrete distributions use is frequently made of the generating functions representing them[21]. We shall assume that the probability of a quantity ξ, assuming values of 1, 2, ..., is p_r when $\xi = r$. The term generating function of a random quantity ξ is applied to the function $G(s) = \sum_r s^r p_r$, where $s \leqslant 1$. The generating function satisfies the self-evident relations

$$G(0) = 0; \quad G(1) = 1.$$

With the aid of generating functions, it is possible to obtain a simple solution of many problems associated with the summation of independent random quantities. Their use makes it possible to replace the complex operation involving the setting up of the distribution functions of random quantities, which is necessary when the latter are added together, by a product of the generating functions of the components. Suppose for example, that ξ and η are independent random quantities. The generating function of the sum of the random quantities $\varphi = \xi + \eta$ is then expressed as follows in terms of the generating functions of the components:

$$G_\varphi(s) = G_\xi(s) \cdot G_\eta(s).$$

The wide-scale employment of the method of generating functions in the calculation of the fundamental MWD parameters is to a large extent associated with the most important property of generating functions, arising from their differentiability and from the existence of simple relations between the nth order moments of the distributions of the random quantities and the nth differential of the generating function. It appears natural to apply the method of generating functions to the calculation of MWD, since the polymer chain length is a typical discrete random quantity. Indeed, at each step of the propagation process, the radical has a number of possible choices: it can continue to grow by interacting with a monomer molecule, or it can participate in a chain transfer reactor, or it can react with other radicals, which leads to their mutual destruction. The employment of the method of generating functions gives rise to a number of significant advantages compared with the classical method. In the first place it makes it possible to eliminate the quasi-stationary hypothesis, which is important in the simulation of radical polymerisation processes up to high degrees of conversion in a periodic-operation reactor, when the polymerisation process is carried out under adiabatic conditions, and in a number of other instances.

The calculation of the MWD by the method of generating functions begins with the usual mathematical treatment of the kinetic mechanism of the polymerisation process. We shall show how the calculation is carried out for the polymerisation in a periodic-operation reactor, considered by Liu and Amundson[20], where

$$w_i = k_i M^n; \; k_f = k_{fs} = 0; \; k_{t_1} = k_{t_2} = k_{t_3} = 0,$$

for the kinetic scheme presented in Table 1. Eqns. (1)–(4) are then written in the following form:

$$\frac{dM}{dt} = -k_i M^n - (k_p + k_{t_3}) MR, \tag{8}$$

$$\frac{dR_1}{dt} = k_i M^n - (k_p + k_{t_3}) MR_1, \tag{9}$$

$$\frac{dR_r}{dt} = k_p R_{r-1} M - (k_p + k_{t_3}) MR_r, \tag{10}$$

$$\frac{dP_r}{dt} = k_t M R_{r-1}; \quad r = 2, 3, \ldots \infty. \tag{11}$$

On multiplying Eqns. (9) and (10) by s^r and carrying out the summation from $r = 1$ to ∞, we obtain

$$\frac{dG}{dt} = sk_i M^n + (k_p s - k_p - k_{t_3}) MG(s). \tag{12}$$

The solution of Eqn. (12) subject to the initial conditions $G(s, t)|_{t=0} = 0$ (i.e. at the initial instant there are no active radicals) yields

$$G(s) = \int_0^t sk_i M^n \cdot \exp\left[-(k_p + k_{t_3}) \int_{t_1}^t M\,dt_2\right] \cdot \exp\left[k_p s \int_{t_1}^t M\,dt_2\right] dt_1. \tag{13}$$

Subsequent expansion of $s \cdot \exp\left(k_p s \int_{t_1}^t M\,dt_2\right)$ in Taylor's series in terms of powers of s in the vicinity of $s = 0$, yields

$$s \cdot \exp\left[k_p s \int_{t_1}^t M\,dt_2\right] = s\left[1 + \frac{sk_p \int_{t_1}^t M\,dt_2}{1!} + \frac{s^2\left(k_p \int_{t_1}^t M\,dt_2\right)^2}{2!} + \ldots + \frac{s^{r-1}\left(k_p \int_{t_1}^t M\,dt_2\right)^{r-1}}{(r-1)!} + \ldots\right] = \sum_r \frac{\left(k_p \int_{t_1}^t M\,dt_2\right)^{r-1}}{(r-1)!} s^r.$$

We substitute this expression in Eqn. (13) and then compare the latter with the definition of the generating function $G(s, t) = \sum_r s_r p_r$. Setting the coefficients of identical powers of s equal to one another, we obtain

$$R_r = k_i \int_0^t M^n \exp\left[-(k_p - k_{t_3}) \int_{t_1}^t M\,dt_2\right] \frac{\left(k_p \int_{t_1}^t M\,dt_2\right)^{r-1}}{(r-1)!} dt_1. \tag{14}$$

In order to calculate $M(t)$, we make use of Eqns. (8) and (12) and the initial conditions

$$M|_{t=0} = M_0, \quad G(1)|_{t=0} = 0.$$

We obtain for $n = 1$

$$\frac{dM}{dG(1)} = -\frac{k_t + (k_p + k_{t_3}) G(1)}{k_t - k_{t_3} G(1)}.$$

Hence

$$M = M_0 + \frac{k_p + k_{t_3}}{k_{t_3}} G(1) + \frac{k_t (k_p + 2k_{t_3})}{k_{t_3}^2} \lg \frac{k_t - k_{t_3} G(1)}{k_t}. \tag{15}$$

Eqn. (11) yields

$$P_r = k_{t_3} \int_0^t MR_{r-1}\,dt_1. \tag{16}$$

Substitution of the expression for R_r from Eqn. (14) and of M from Eqn. (15) in Eqn. (11) gives the required distribution $P = f(r)$.

The formulae for the calculation of the MWD by the method of generating functions in the given case for other radical polymerisation mechanisms are not as cumbersome as might have been expected when the Bodenstein–Semenov hypothesis is abandoned. The introduction of generating functions made it possible to replace an infinite system of differential equations (9) and (10) in terms of

ordinary derivatives by a single first-order differential equation (12), also in terms of ordinary derivatives. This considerable advantage of the method led to its wide scale employment in studies of the mathematical simulation of radical polymerisation[20,22-24].

The principal statistical characteristics of the distribution—its moments—frequently permit more clear-cut inferences about the form of the distribution than does the knowledge of the analytical expression for the MWD and their calculation is much easier than the calculation of the MWD itself. The relation between the moments of the distribution and the generating function for $s = 1$ in the following way:

$$\mathcal{M}_1 = \sum_r rP_r = \frac{dG}{ds}\Big|_{s=1},$$

$$\mathcal{M}_2 = \sum_r r^2P_r = \mathcal{M}_1 + \frac{d^2G}{ds^2}\Big|_{s=1}.$$

The application of the method of generating functions yields compact analytical expressions for the number-average (μ_1) and weight average (μ_2) molecular weights of the polymers. Suppose that

$$G(s) = \sum_n s^n R_n,$$

$$H(s) = \sum_n s^n P_n$$

are the generating functions of the concentration of free radicals and the polymer. Consider a function $F(s) = G(s) + H(s)$. The number-average and weight-average molecular weights can then be expressed as follows in terms of the derivative functions $F(s)$:

$$\mu_1 = \frac{\sum_n nR_n + \sum_n nP_n}{\sum_n R_n + \sum_n P_n} = \frac{d \ln F(1)}{ds},$$

$$\mu_2 = \frac{\sum_n n^2R_n + \sum_n n^2P_n}{\sum_n nR_n + \sum_n nP_n} = 1 + \frac{d^2F(1)}{ds^2} \Big/ \frac{dF(1)}{ds}.$$

Higher-order moments can be calculated by a similar use of the derivative functions $F(s)$. The function $F(s)$ is found as the solution of a system of equations set up for any reactor (individual or in a reactor cascade) using the technique of generating functions.

IV. THE CONTINUOUS VARIABLE METHOD

The application of the method of generating functions to the calculation of the MWD or a finite number of its moments is limited to the region where the assumption of the invariance of the chain propagation and termination rate constants holds regardless of the length of the molecular chain. The principle of the independence of the reactivity of the terminal or any other group of the polymer molecule of its length does not hold in many instances, for example, in polymerisation in highly dilute solutions.

The continuous variable method makes it possible to calculate the MWD without adopting the drastic simplifying assumption that the rate constants for the elementary reactions are independent of the molecular chain length. The principal idea of the method involves the approximate representation of the mathematical problem with an infinite number of discrete variables by a continuous problem. An attempt at such an approximation would be natural for any mathematical system involving an infinite number of discrete variables. These considerations enabled Zeman and Amundson[25-27] and Thiele et al.[28] to treat the concentration of polymer molecules with a length P_r in the calculation of the MWD not as a function of a discrete variable r but as a function of a continuous variable $P(r)$. From the physical standpoint, this is a very satisfactory approximation, since the change in length by unity can be regarded as fairly small for fairly long chains.

The continuous variable method will be demonstrated in relation to the calculation of the MWD in radical polymerisation[25], where the reaction is carried out in a continuous-operation reactor via the following kinetic mechanism (Table 1).

$$k_f = k_{s_1} = 0, \quad k_{t_1} = k_{t_2} = k_{t_4} = 0, \quad w_i = k_i M.$$

We shall abandon the hypothesis that the rate constants for the chain propagation and termination reactions are independent of chain length. In this case the equations for the stationary state are

$$M_0 - M\left[1 + k_t\theta + \theta\sum_r k_{p_r}R_r + \theta\sum_r k_{t_r}R_r\right] = 0, \tag{17}$$

$$-R_1[1 + \theta k_{p_1}M + \theta k_{t_1}M] + \theta k_i M = 0, \tag{18}$$

$$-R + k_t\theta M - \theta M\sum_r k_{t_r}R_r = 0, \tag{19}$$

$$-P_r + k_{t_{r-1}}\theta M R_{r-1} = 0, \tag{20}$$

$$-R_r + \theta M(k_{p_r}R_r - k_{p_{r-1}}R_{r-1}) - \theta M k_{t_r}R_r = 0,$$
$$r = 2, 3, \ldots \infty. \tag{21}$$

We shall use the fundamental relations of the continuous variable method:

(a) Suppose that the propagation and termination rate constants are known functions of chain length: $k_p = k_p(r)$ and $k_t = k_t(r)$;

(b) A relation between the continuous variable $R(r)$ and a function of the discrete variable R_r is established with the aid of the Euler–Maclaurin formula[29]:

$$R = \sum_r R_r = \int_1^\infty R(r)\,dr + \frac{R(1) + R(\infty)}{2},$$

where $R(1) = R_1$ by definition and $R(\infty) = 0$ from physical considerations; there is a zero probability of the appearance of a concentration of a polymer with an infinite chain length;

(c) The expansion of $R(r-1)$ in Taylor's series, neglecting terms with orders of smallness higher than the first, yields correspondingly

$$R(r-1) = R(r) - \frac{dR(r)}{dr}.$$

After changing to a continuous variable, the system of Eqns. (17)–(21) becomes

$$M_0 - M\left[1 + k_t\theta + \theta\int_1^\infty k_p(r)R(r)\,dr + \theta\int_1^\infty k_t(r)R(r)\,dr + \right.$$
$$\left. + \frac{\theta}{2}[k_p(1) + k_t(1)]R(1)\right] = 0, \tag{17'}$$

$$R(1) = \frac{k_i\theta M}{1 + \theta[k_p(1) + k_t(1)]M}, \tag{18'}$$

$$R = k_i\theta M - \theta M\int_1^\infty k_t(r)R(r)\,dr - \frac{1}{2}\theta k_{t_1}MR(1), \tag{19'}$$

$$P(r) = \theta k_t (r-1)\, MR(r-1), \qquad (20')$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[k_p(r)\,R(r)] + \frac{1+\theta M k_t(r)}{\theta M} R(r) = 0, \quad r \geqslant 2. \qquad (21')$$

Eqn. (21′) can be integrated after obtaining an expression for the distribution of active radicals:

$$R(r) = \frac{k_{p_1}}{k_p(r)} R(1) \exp\left(-\int_1^r \alpha(r)\,\mathrm{d}r\right); \quad r \geqslant 1, \qquad (22)$$

where $\alpha(r) = [1 + \theta k_t(r)M]/\theta M k_p(r)$ and $R(1)$ is defined by Eqn. (18′). After substituting Eqn. (22) in Eqn. (20′), we obtain an expression for the distribution of polymer molecules with respect to chain length:

$$P(r) = \theta M R(1)\, k_{p_1} \frac{k_t(r-1)}{k_p(r-1)} \exp\left[-\int_1^{r-1} \alpha(r)\,\mathrm{d}r\right]; \quad r \geqslant 2\,. \qquad (23)$$

In order to calculate the distribution by Eqn. (23), it is first necessary to find M. For this, one must substitute $R(1)$ from Eqn. (18′) and $R(r)$ from Eqn. (22) in Eqn. (17′) and the resulting expression must then be solved for M. In the given calculation of the MWD one must postulate that the chain propagation and termination rate constants depend on the chain length instead of the assumption that the reactivity of the radicals is constant, which was abandoned at an earlier stage. A linear relation between the activation energies for elementary chain propagation and termination reactions and chain length was adopted[26]. A relation has been proposed[14] between the chain propagation rate constant and the molecular weight of the polymer molecule.

A simple case, where the chain propagation and termination rate constants are independent of chain length, follows from Eqns. (17′)–(21′). Eqns. (17′)–(21′) can then be written as follows:

$$M_0 - M[1 + k_i\theta + \theta(k_p + k_t)R] = 0, \qquad (17'')$$

$$R(1) = \frac{\theta k_i M}{1 + \theta(k_t + k_p)M}, \qquad (18'')$$

$$P(r) = \theta k_t M R(1) \exp[-\alpha(r-2)], \qquad (19'')$$

$$R = \frac{\theta k_i M}{1 + \theta k_t M}, \qquad (20'')$$

$$R(r) = R(1)\exp[-\alpha(r-1)], \quad \alpha = [1 + \theta k_t M]/\theta k_p M. \qquad (21'')$$

Hence we find the distribution of the active radicals and polymer molecules:

$$R(r) = R(1)\exp[-\alpha(r-1)], \qquad (22'')$$

$$P(r) = \theta k_t R(1)\exp[-\alpha(r-2)]. \qquad (23'')$$

The use of the continuous variable method for a periodic-operation reactor will be demonstrated by the following example: suppose that chain termination takes place only via the monomer, i.e. in Table 1 $k_{t_1} = k_{t_2} = k_{t_4} = 0$, there is no chain transfer reaction ($k_f = k_{f_S} = 0$), and the rate constants for the elementary reactions are invariant. The rate equations for the variation of the concentrations of the active polymer radicals assume the following form in the case under consideration:

$$\frac{\mathrm{d}R_r}{\mathrm{d}t} = -k_p M(R_r - R_{r-1}) - k_t M R_r; \quad R_r(0) = 0; \quad r = 2, 3, \ldots \infty. \qquad (24)$$

On changing to a continuous variable, this infinite system of differential equations with ordinary derivatives can be transformed into a single equation in terms of partial derivatives:

$$\frac{\partial R(r,t)}{\partial t} = -k_p M \frac{\partial R(r,t)}{\partial r} - k_t M R(r,t); \quad R(r,0) = 0; \quad R(1,t) = R_1(t); \quad r \geqslant 2. \qquad (25)$$

Similarly the infinite system of differential equations in terms of ordinary derivatives, which describes the rate of change of the concentrations of inactive molecules,

$$\frac{\mathrm{d}P_r}{\mathrm{d}t} = k_t M R_{r-1}, \quad P_r(0) = 0; \quad r = 2, 3, \ldots \infty \qquad (26)$$

is transformed, within the framework of the continuous variable method, into a single partial differential equation:

$$\frac{\partial P(r,t)}{\partial t} = k_t M R(r,t), \quad P(r,0) = 0; \quad r \geqslant 2. \qquad (27)$$

Thus, with the aid of the continuous variable method, the infinite system of algebraic material balance equations for a continuous-operation reactor can be reduced to a single differential equation and the infinite system of differential equations describing the non-stationary state of the polymerising system in a periodic-operation reactor is reduced to several partial differential equations.

V. POLYMERISATION AT HIGH CONVERSIONS

The mathematical methods for the calculation of the MWD examined above are applicable mainly to radical polymerisation processes occurring up to low degrees of conversion of the monomer. At high conversions the analytical relations for the rate of polymerisation, obtained by considering the classical kinetic mechanism, lead to appreciable discrepancies with experiment: virtually none of the mechanisms reproduces the experimental dependence of the rate of polymerisation of styrene on the degree of conversion obtained by one of the present authors and his coworkers[37]. The majority of polymerisation processes, particularly industrial processes, are continued up to high degrees of conversion. At high conversions the rate constants for the elementary reactions can no longer be regarded as constant[6,26,38]. An increase of the viscosity of the reaction medium during polymerisation is known to have a major influence on the rate of the chain termination reaction; however, there is no doubt about the influence of this factor also on the rates of other elementary reactions.

The form of the distribution function associated with the changes in these constants varies with the degree of conversion. At high conversions another simplification postulating that the radical concentrations are quasi-stationary, does not hold either. The point is that at high conversion one should expect a considerable increase of the lifetime of polymer radicals and hence also of their concentration, since radicals become relatively immobile in a highly viscous medium and cannot be destroyed as a result of interactions. The adoption of the Bodenstein–Semenov hypothesis would lead to an appreciable error in this instance. The above factors greatly complicate the kinetic calculation of the MWD at high conversions. On the other hand, polymerisation processes continued up to high degrees of conversion of the monomer are in fact of practical interest for the solution of many problems in the industrial application of the process: in the selection of a

technological scheme and type of reactor and in the calculation of the optimum technological conditions.

Isolated studies concerned with quantitative descriptions of radical polymerisation at high conversions have been carried out recently. One of the methods for the theoretical calculation of the MWD in radical polymerisation at high conversions has been proposed by Graessley et al.[39] It is based on the recognition and allowance for an important factor—the dependence of the rate constants for the elementary reactions on the degree of conversion. In order to simplify the problem, the author disregarded the remaining factors. A parameter, defined as the average number of units contained in the growing chain from the instant of its formation in the initiation of radicals up to deactivation on chain transfer or termination, was introduced:

$$\lambda = \frac{w_p}{w_f + w_{fS} + w_{t_1} + w_{t_2} + w_{t_3} + w_{t_4}}.$$

Since the rate constants for the elementary reactions vary with the degree of conversion, the parameter λ reflects these changes: $\lambda = \lambda(C)$, where C is the degree of conversion of the monomer. This exhausts the kinetic approach and the author[39] turns to a purely statistical treatment. In particular, he assumes that the growing molecules obey an exponential distribution law with respect to lengths:

$$f_r(C) = \frac{1}{\lambda} \exp\left(-\frac{r}{\lambda}\right).$$

In polymerisation in a periodic-operation reactor the total number of chains formed for an increment in the degree of conversion ΔC is proportional to $\Delta C/\lambda(C)$. Then the fraction of molecules with a chain length r, present for a degree of conversion C, is

$$F_r(C) = \int_0^C f_r(\xi) \frac{\mathrm{d}\xi}{\lambda(\xi)} \Big/ \int_0^C \frac{\mathrm{d}\xi}{\lambda(\xi)}.$$

Thus the characteristics of the polymerisation are taken into account exclusively by the parameter λ. The proposed method employs to a significant extent fairly drastic simplifications, which to some extent obliterate the characteristic features of polymerisation at high conversions. The influence of disregarded factors is in no way smaller than the variation of the rate constants for the elementary reactions with the degree of conversion, which has been taken into account.

An interesting approach to a quantitative description of polymerisation has been proposed[40]. Assuming that all the characteristics of the thermally initiated polymerisation of styrene in bulk which lead to discrepancies between theory and experiment at high conversions can be accounted for by changes in the rate constants for the elementary reactions, the constants are calculated on a computer by means of the following equations:

$$w(k_i, k_t, k_p) = w^{\mathrm{emp}}(C, T), \quad (28)$$

$$P_N(k_i, k_t, k_p, k_f) = P_N^{\mathrm{emp}}(T), \quad (29)$$

where $w(k_i, k_t, k_p)$ and $P_N(k_i, k_t, k_p, k_f)$, the theoretical expressions for the rate of reaction and the number-average degree of polymerisation as a function of the rate constants for the elementary reactions, are set equal to the simpler equivalent empirical expressions $w^{\mathrm{emp}}(C, T)$ and $P_N^{\mathrm{emp}}(T)$. An expression from the paper of Gleizer et al.[37] was adopted as the empirical equation for the rate of reaction $w(C, T)$:

$$w(C, T) = k_0 \exp[-E/RT] f(C), \quad (30)$$

where C is the degree of conversion and $f(C)$ an empirical function; the following expression is fitted to the experimental relation $P_N(T)$:

$$P_N(T) = a_N \exp[b_N/T]. \quad (31)$$

The rate constants for the elementary reactions obtained from Eqns. (28) and (29) are introduced into the theoretical equations for all the required MWD moments.

The above approach is analogous to the earlier method[41] for the solution of the converse problem involving the determination of the elementary rate constants as a function of temperature and the degree of conversion by minimising the Bayes factor[42]. The mathematical model of the MWD of the polymer obtained in the thermally initiated polymerisation of styrene was based on the kinetic mechanism for radical polymerisation with chain transfer to the monomer and the adduct, chain termination by recombination, and two different initiation mechanisms (with second and third orders with respect to the monomer). Equations for the rates of variation of the concentration of the active and inactive radicals and the monomer were set up in the traditional manner for the case under consideration. With the aid of the method of generating functions, the infinite system of ordinary differential equations in terms of the rate of variation of the concentration of polymer radicals (active and inactive) was converted into two ordinary differential equations in terms of generating functions of the concentrations of free radicals $[G(s)]$ and the polymer $[H(s)]$. Analytical expressions for the number-average and weight-average molecular weights can be obtained from these equations as a function of the rate constants for the elementary reactions. Empirical formulae relating the latter to the degree of conversion have been proposed. In the determination of the unknown coefficients in these formulae the authors[41] used one of the identification algorithms[42], which was executed using the experimental points representing the changes in the degree of conversion and in the number-average and weight-average molecular weights with time under isothermal conditions.

The essential feature of the method is that one has to find m unknown parameters θ_n ($n = 1, 2, \ldots, m$) from n observed values of Y_{iu} ($i = 1, 2, \ldots, k$; $u = 1, 2, \ldots, n$) (i.e. from n measured degrees of conversion and number-average and viscosity-average molecular weights) of the function $f_i(X_{iu}^g, \theta_n)$, the form of which is known:

$$Y_{iu} = f_i(X_{iu}^g, \theta_n) + \varepsilon_{iu},$$

where X_{iu}^g (with $i = 1, 2, \ldots, k$; $u = 1, 2, \ldots, n$; $g = 1, 2, \ldots, r$) represents r variables corresponding to n observations for each ith constituent vector-function and ϵ_{iu} is the error of the observation.

The relations obtained for the rate constants, which take into account all the characteristics of the polymerisation at high conversions, enabled the authors[41] to carry out a theoretical computer calculation of the MWD of polystyrene obtained in thermally initiated polymerisation. Fig. 4 reveals a fairly satisfactory agreement between the theoretical and experimental MWD curves. Table 3 shows that the fundamental experimental and calculated MWD parameters also proved to be fairly close. The mathematical model for the MWD of a polymer obtained by radical polymerisation (continued up to virtually complete

conversion of the monomer), proposed in the study under consideration, is of undoubted interest for the planning and optimisation of industrial polymerisation processes.

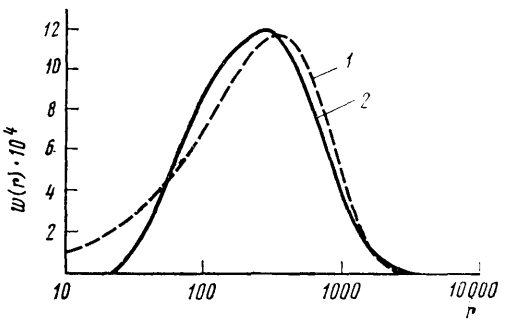


Figure 4. Comparison of the MWD obtained for a high degree of conversion of the monomer under isothermal conditions[41]: 1) calculated; 2) experimental.

Table 3. Comparison of the calculated and experimental MWD parameters at high conversion (X_{calc} = 95.1%, X_{exp} = 95.9%) on the basis of the data of Hui and Hamielec[41].

MWD parameter	Calculated value	Experimental value
M_n	35 000	35 500
M_w	70 600	71 200

VI. CALCULATION OF THE MOLECULAR WEIGHT DISTRIBUTION IN THE PRODUCTION OF HOMOPOLYMERS IN A CASCADE OF REACTORS

The study of the MWD at the output end of a cascade of polymerisation reactors merits particular attention, because a reactor cascade constitutes the most suitable technical means for carrying out polymerisation which permits a stepwise alteration of the temperature and concentration of the reactants, i.e. a stepwise alteration of the polymerisation conditions from the reactor to reactor.

For a cascade of Λ ideal mixing flow reactors, in which the polymerisation reaction takes place in accordance with the mechanism presented in Table 1 with $k_f = 0$ and $k_{t_2} = k_{t_4} = 0$, a system of algebraic equations defining the function $F(s) = G(s) + H(s)$ is set up by the generating function method:

$$M(n) = \frac{M(n-1) - \theta_n k_i(T_n) I_n}{1 + \theta_n \{[k_p(T_n) + k_f(T_n)] G(1, n) - k_f(T_n) R_1(n)\}}$$

$$R_1(n) = \frac{R_1(n-1) + \theta_n \{k_i(T_n) I_n + k_f(T_n) M(n) G(1, n)\} s}{1 + \theta_n \{M(n)[k_p(T_n) + k_f(T_n)] + k_i(T_n) G(1, n)\}}$$

$$G(s, n) = \frac{G(s, n-1) + \theta_n \{k_i(T_n) I_n + k_f(T_n) M(n) G(1, n)\} s}{1 + \theta_n \{M(n)[k_p(T_n)(1-s) + k_f(T_n)] + k_{t_1}(T_n) G(1, n)\}}$$

$$H(s, n) = H(s, n-1) + \theta_n \left\{\frac{k_{t_1}(T_n)}{2} G(s, t)^2 + k_f(T_n) M_n [G(s, n) - sR_1(n)]\right\}.$$

$$n = 1, 2, \ldots N.$$

The elimination of computational difficulties, associated with the calculation of the moments of the MWD function, with the aid of the derivative functions $F(s)$ (see Section III) makes it possible to formulate and solve the problem of the optimisation of ideal mixing polymerisation flow reactors taking into account the quality of the polymer obtained. Ray and coworkers[22,23] made the first attempt at the optimum design of the polymerisation process in a cascade of chemical reactors in order to obtain the required MWD parameters for the polymer. In this case the problem reduces to the determination of the optimum polymerisation conditions by an appropriate choice of the initiator concentration, temperature, and the residence time of the polymerising mass in the reaction system. A linear function of the standard of deviations of the principal MWD parameters and of the degree of conversion from the required values of the latter is adopted as a criterion which determines whether or not optimum conditions have been obtained:

$$f = (\mu_1 - \bar{\mu})^2 + \lambda_1 \left(\frac{\mu_2}{\mu_1} - \bar{S}\right)^2 + \lambda_2 (1 - C)^2,$$

where λ_1 and λ_2 are the weighting factors taking into account the relative importance of the polydispersity and the degree of conversion of the finished product and $\bar{\mu}$ and $\bar{S}$ are the required molecular weight and polydispersity coefficient respectively. The optimum conditions for the polymerisation process were calculated on a computer in relation to the polymerisation of styrene in one flow reactor or in a cascade of two reactors. The calculations were performed for different versions of the requirements imposed on the width of the MWD (for the minimum width of the MWD, $\bar{S} = 1$; for a wider distribution, $\bar{S} = 3$), the weighting factors of the components of the above criterion being varied by altering the ratio λ_1/λ_2. The calculations yielded the optimum values of the technological parameters ensuring the maximum degree of conversion and the minimum polydispersity of the polymer.

The continuous variable method has found extensive applications in calculations of the MWD in radical polymerisation processes in a cascade of reactors of different types. The MWD for polystyrene has been calculated[8] taking into account chain transfer to the monomer and chain termination by recombination in continuous-operation reactors. The authors[8] compared two methods for the theoretical calculation of the MWD and observed that the MWD curve calculated by the continuous variable method virtually coincides with the distribution curve calculated by the classical method. For the same initial conditions and the same average residence time, a comparison was made in the same study of the MWD for one-, two-, and three-cascade polymerisation processes. In the calculation of the MWD for the polymer in a reactor cascade the advantage of the continuous variable method over the classical method is particularly manifest; for a cascade of three isothermal reactors, the classical method is already unsuitable even when computers are used, whereas with the aid of the continuous variable method the computational difficulties can be fully overcome.

Calculations on the cascade method of industrial polymerisation with intermediate injection of the initiator can also be performed by the continuous variable method. The influence of various reaction conditions on the MWD of polystyrene has been calculated in relation to the initiated polymerisation of styrene[30]. The calculations showed that, by altering the process conditions (reaction temperature, residence time of the polymerising mass in the reactors, initial monomer concentration, and the

intermediate supply of the initiator, monomer, and solvent), it is possible to affect the MWD appreciably. Hence we believe that a natural step to take would involve optimum planning of the polymerisation process in order to obtain a finished product with specified properties, subject to the condition that the relation between the physicomechanical properties of the polymer and the MWD [31-36] is expressed in a mathematical form. Although exact correlations between the MWD and the physicomechanical properties of polymers have not as yet been established, there now exist many empirical and qualitative relations which can be used in the optimisation and planning of the industrial technological process under conditions where these properties depend on the MWD.

A combination of theoretical equations for the MWD parameters with empirical equations has been used[43-45] to describe the rate of an industrial polymerisation process in order to optimise the thermally ionised polymerisation of styrene in a continuous-operation apparatus consisting of N series-connected isothermal ideal mixing reactors and a reactor of the column type. The stationary state of thermally initiated block polymerisation of styrene was described, taking into account the non-ideality of the flow of the polymerising mass in the column, by a system of algebraic and differential equations. The mathematical description of the process is based on the representation of the rate of polymerisation by the product of two functions, one of which characterises the dependence of the rate on temperature and the other its dependence on the degree of conversion:

$$w(T, C) = w_0(T) f(C).$$

The term expressing the temperature dependence is described by the Arrhenius law

$$w_0(T) = k_0 \exp(-E/RT),$$

and $f(C)$ is specified by an empirical curve constructed on the basis of experimental data and showing how the rate of polymerisation decreases relative to the initial rate of polymerisation $w_0(T)$ at the same temperature as the degree of conversion increases.

Relations obtained on the basis of the definition of the number-average and weight-average molecular weights as the ratios of the corresponding moments of the MWD function have been proposed for the calculation of the principal characteristics of the MWD (see Section III). The presence of an empirical element in the proposed[43-45] mathematical model of the thermally initiated block polymerisation of styrene in a cascade of industrial reactors of different types deprives this approach of the generality characteristic of a purely theoretical calculation; however, the approach permitted a simple and effective solution of the specific problem of the optimum connection of reactors and of the search for the optimum operating conditions of an industrial polymerisation apparatus. Fig. 5 presents a diagram illustrating the technological conditions calculated using digital computers on the basis of algorithms and models developed by Gleizer and coworkers[37,43-45]. The region with the smallest polydispersity is located in the upper right-hand corner of the diagram. The optimum technological parameters selected from this region (the degree of conversion in the first reactor C_1, the temperature in the first reactor T_1, and the temperature in the second reactor T_2) ensure the minimum residence time of the polymerisation mass in the reactor cascade (τ) and the minimum polydispersity of the final polymer (μ_f) for fixed requirements to be met by the final degree of conversion of the finished product (C_f) and its viscosity-average molecular weight (M_f).

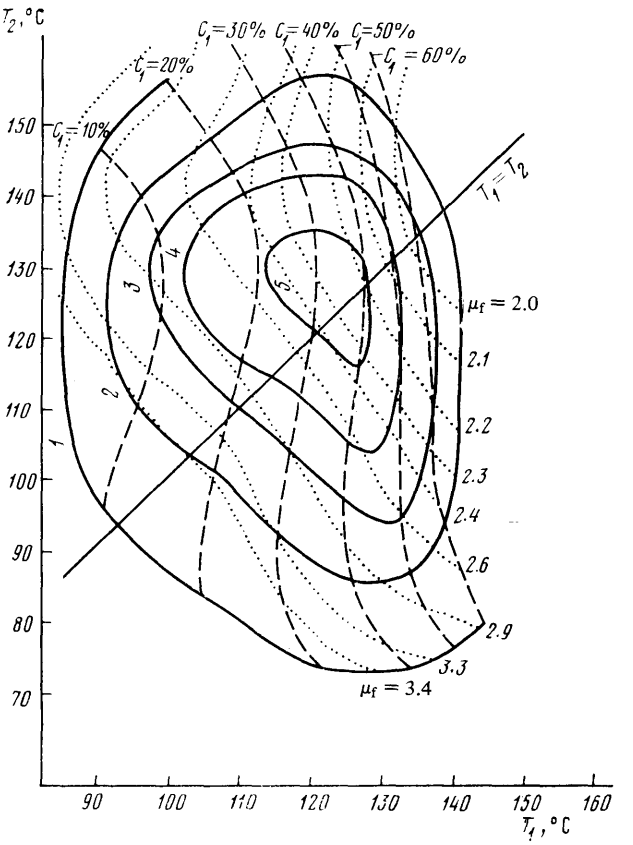


Figure 5. Diagram of technological conditions for the polymerisation of styrene in a cascade of reactors[45] (M_f = 350 000; C_f = 98%): overall residence time of the polymerising mass in the system $\Sigma\tau$ (hours): 1) 15; 2) 10; 3) 8; 4) 7; 5) 6.

Hitherto calculations have been made on polymerisation reactions which can occur both in an individual reactor and in a technological apparatus consisting of series-connected reactors. The type of reactors and the sequence in which the polymerising mass passes through them were assumed to be specified. However, in the development of a technological polymerisation process one of the problems is in fact the selection of the optimum polymerisation system. Evidently the type of reactors and the method of their connection have a significant influence on the degree of reaction of the initial monomer and the composition of the polymer produced. The study where an advance was made towards the next level of the investigation of polymerisation reactors on the basis of their kinetic models—the creation of a polymerisation system of reactors on the basis of a criterion whose optimisation ensures the best functioning of the system—is therefore of interest[24]. This problem must be solved using apparatus for the

polymerisation reaction comprising only one reactor. It is known that, for all reactions (including polymerisation reactions) whose order is positive, a higher degree of conversion of the initial product is attained in a periodic-operation reactor than in an ideal mixing flow reactor with the same reaction volume. The absence of the mixing of the reaction mixture with a fresh stream of the initial monomer in the periodic-operation reactor, of the kind that takes place in a flow reactor, makes the average rate of reaction in the latter always lower than in a periodic-operation reactor. However, in ideal mixing flow reactors processes at higher monomer concentrations take place more effectively. On the other hand, a narrower MWD is frequently obtained in a periodic-operation reactor than in a flow reactor (for example, when the lifetime of the active radical is comparable to the residence time in the reactor[7]).

Industrial polymerisation processes take place up to high conversions and it is desirable to investigate a narrow MWD. Taking into account the nature of the flow of the reaction mixture through the reactors, it is therefore important to arrange them in the following sequence: one or several continuous-operation reactors in the form of fore-polymerisers followed by a displacement reactor (or a periodic-operation reactor) which ensures a high degree of conversion of the monomer. However, even for a system consisting of only two reactors, one of which is of the flow type and the other is of the periodic-operation type, it is not easy to solve the problem of the redistribution of the stream between the reactors, the additional injection of reactants at intermediate stages, and the recycling of part of the stream. Examination of these features from the standpoint of their influence on the degree of conversion and the MWD requires calculations on numerous versions using mathematical models of polymerisation reactors. The addition to a single flow reactor of a further series-connected device, which leads to a higher degree of conversion of the initial monomer, increases sharply the number of versions for which calculations must be made in order to select the optimum conditions. The problem arises of the development of computer algorithms which permit calculations, on the basis of mathematical models of polymerisation reactors, for different versions of the schemes for their connection and a choice of one of them in terms of a criterion.

The scalar function

$$\mathcal{K} = \alpha_1 M + \alpha_2 (\sigma - \bar{\sigma})^2 + \alpha_3 (\Delta - \bar{\Delta})^2,$$

where M is the monomer concentration at the outlet from the polymerisation system, $\bar{\sigma}$ and $\bar{\Delta}$ are the specified degree of dispersion and the mathematical expectation of the MWD function, and α_i (where $i = 1, 2, 3$) are weighting factors, has been proposed as a criterion[24]. The minimisation of the function $\mathcal{K}(M, \sigma, \Delta)$ ensures the attainment of the maximum degree of conversion of the monomer and the minimum deviation of the zeroth, first, and second moments of the MWD from their specified values at the outlet from the system.

We shall now analyse the procedure for the selection of the optimum system of reactors from the multiplicity of permissible systems on the basis of the criterion proposed[24]. For a more detailed analysis of the existing versions and the elucidation of ways of applying the proposed methods, we shall consider initially a technological scheme comprising two series-connected reactors: an ideal mixing flow reactor (FR) and a periodic-operation reactor (POR). We shall consider all possible ways of connecting the FR and the POR for a fixed overall reaction volume of the system. They give rise to a multiplicity of structures of the reaction system and the optimum structure is in this case selected as follows. In the first place, for each stream mixing point, material balance equations with respect to the initiator and the monomer and the equations for the calculation of the MWD moments at the stream merging points from the moments in each of the streams being mixed are set up.

In order to calculate the moments, one sets up with the aid of the generating function method a kinetic model of the initiated radical polymerisation taking into account the chain propagation reaction and chain termination by recombination. The kinetic equations supplemented by stream material balance equations form a universal mathematical model describing various structures of the reaction system. With the recirculation coefficients varied from 0 to 1 (which thus leads to a selection of various structural versions of the reaction system), this model permits computer calculations of all possible structural versions for different requirements to be met by the resulting polymer (by fixing a set of weighting factors for the optimum conditions criterion).

On the basis of these calculations, the structural features of the given reaction system are established. In the first place, it was found that the recirculation of a large proportion of the stream is undesirable, since it leads to an appreciable increase of the target function. The recirculation of very small proportions of the streams in the organisation of the reaction system must be ruled out in view of their insignificant influence on the process, which is expressed by the virtually unchanged values of all the components of the target function. The recirculation of the stream both from the outlet of the FR and from the outlet of the POR to the inlet of the FR is undesirable, since it leads to an increase of the target function owing to the increase of the monomer concentration at the outlet from the system due to the decrease of the overall residence time of the polymerising mass in both reactors. The deviation of the variance and of the mathematical expectation of the MWD function from the specified values then decreases only slightly owing to the mixing of the molecules, emerging from the outlet during the process, with the incoming molecules (the former thus acquire some, albeit small, capacity for growth).

An optimum structural version has been proposed for the polymerisation system under consideration: series-connection of the FR and POR, which are bypassed by a fraction of the streams (0.336 and 0.704 respectively) and in which the ratio of the POR and FR volumes is 0.294. The influence of the changes in the rate constants for the elementary reactions on the polymerisation process has been analysed for the optimum system obtained. A study was also made of the influence of the temperature conditions on the given polymerisation process in this system. For this purpose, the POR was subdivided into two temperature zones. The consequent increase of the target function is associated with the improvement of the MWD parameters.

The methods for the investigation of processes involved in the production of homopolymers, which were considered here on the basis of a mathematical description of the MWD, give rise to considerable possibilities for the analytical development (with the aid of computers) of new polymerisation processes, the theory of calculations on chemical reactors and of the mathematical simulation of the MWD being related to the technological apparatus for the polymerisation processes.

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Activators of the Anionic Polymerisation of Lactams

T.M.Frunze, V.V.Kurashev, V.A.Kotel'nikov, and T.V.Volkova

The influence of the structure of activators on the anionic polymerisation of lactams is examined and a classification of activators taking into account the chemical nature of the active centres formed and the side products is proposed. An approach to the specific selection of activating compounds for the regulation of the rate of polymerisation is described and the possibility, in principle, of employing activators with different functionalities for varying the structure and properties of the resulting polyamides is demonstrated. Data are presented on the modification of polyamides using macromolecular activators of the anionic polymerisation of lactams.
The bibliography includes 210 references.

CONTENTS

I. Introduction 991
II. The polymerisation mechanism 991
III. Classification of activators 992
IV. The influence of the chemical structure of activating compounds on their efficiency 995
V. The influence of the functionality of activators on the molecular structure of the polymers formed 998
VI. Macromolecular activators of the anionic polymerisation of lactams 1000

I. INTRODUCTION

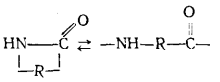
Among the industrial methods for the synthesis of polyamides, the polymerisation of lactams occupies a notable place. Thus, one of the most important and widely used examples of the class of polyamides, namely polycaproamide, is obtained on an industrial scale mainly by the hydrolytic polymerisation of ϵ-caprolactam.

When the activating influence of imides, the so-called activators, on the anionic polymerisation of lactams was established, the polymerisation of cyclic amides became even more important. The use of activators in the anionic polymerisation of lactams led to the development of a virtually new method for the synthesis of polyamides and articles made from them—by activated anionic polymerisation. By greatly reducing the energy expenditure, this method makes it possible to obtain articles by chemical moulding involving a "monomer–finished article" procedure. In view of the absence of the processing stage, a unique possibility is created for the formation of large articles of various configurations.

Numerous papers devoted to activating systems in the anionic polymerisation of lactams have been published. The aim of the present review is to give a systematic count of accumulated data, to examine the influence of the chemical structure of compounds of different types on their activating capacity in the anionic polymerisation of lactams, and to consider the possibility of using activators for the regulation of the molecular structure of the polyamides formed.

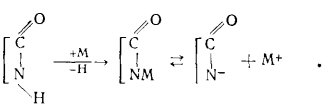
II. THE POLYMERISATION MECHANISM

The capacity of lactams of different structures for polymerisation is determined by thermodynamic and kinetic factors. It has now been established that the opening of the amide ring at the heterobond



is a thermodynamically favourable process for virtually all the known unsubstituted lactams, although the position of the thermodynamic equilibrium for each monomer depends on its chemical structure [1]. The possibility of obtaining a high-molecular-weight polymer is determined not only by the thermodynamic but also by the kinetic stability of the ring, i.e. its reactivity. The latter depends on a whole series of factors, among which the following may be mentioned: the resonance stabilisation of the amide linkage within the lactam ring, the conformation of the macromolecules (the presence of *cis*- and *trans*-isomers), the possibility of the formation of intermolecular hydrogen bonds, and the basicity of the monomer [1-5]. In addition, the kinetics of the overall polymerisation process depend to a large extent on the nature of the catalytic system used.

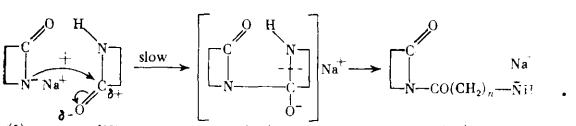
Being weak bases, lactams form salts when they interact with alkali metals, alkali metal and alkaline earth metal hydrides and amides, and organometallic compounds:



The anions formed on dissociation of salts catalyse the polymerisation of lactams.

The following mechanism of the anionic polymerisation of lactams can now be regarded as established [5-15]:

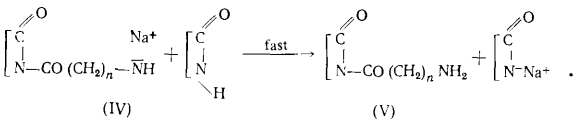
(a) The nucleophilic attack by the anion of lactam (I) on the carbonyl carbon atom of the monomer (II) results in the formation of the intermediate carbinolate anion (III), which is stabilised when the ring is opened with formation of the N-anion (IV)



(I) (II) (III) (IV)

(b) In contrast to the lactam anion, the anion of a primary amine is not stabilised. The N-anion (IV) is therefore highly reactive and rapidly reacts with the monomer, abstracting a proton from the latter. The driving force of this reaction is the appreciable difference

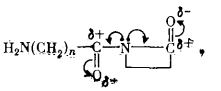
between the acidities of the amino- and amido-groups:



(IV) (V)

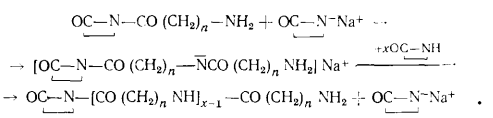
The imide dimer (V) (an *N*-substituted acyl-lactam) formed activates the propagation of the macromolecular chain.

The presence of two carbonyl groups linked to the nitrogen atom in the imide structure leads to a decrease of the resonance stabilisation of the amide linkage within the lactam ring (imide mesomerism):



which promotes an appreciable increase of the activity of the carbonyl group of the cyclic amide in relation to the nucleophilic lactam anion.

(c) Chain propagation is a reaction between the imide molecule and the lactam anion followed by a rapid proton exchange with the monomer, the anion and the terminal imide group of the growing polymer chain being regenerated in each addition step:



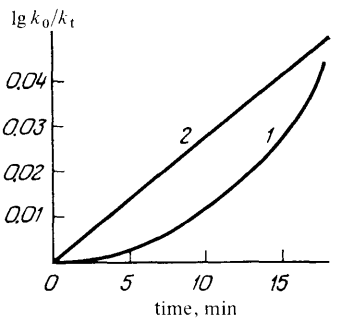
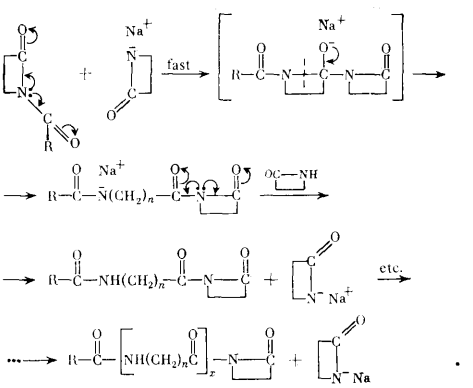


Figure 1. The rate of the anionic polymerisation of ε-caprolactam at 192.6°C in the presence of various additives: 1) 0.5 mole % of the sodium salt of ε-caprolactam; 2) 0.5 mole % of the sodium salt of ε-caprolactam and 0.5 mole % of tetra-acetylhexamethylenediamine[16].

The polymerisation of lactams in the presence of alkaline catalysts takes place with an appreciable induction period[16] (Fig. 1, curve *1*).

Presumably this is associated with the high activation energy for the formation of reactive compounds having the imide structure and the introduction of such compounds into the reaction system should activate the polymerisation process. This hypothesis has been confirmed by Ney and Grouther[17] and then by Šebenda and Kraličeк[16,18], who showed that the use as activators of acyl-lactams, acid chlorides, ethers, and esters, i.e. compounds containing the imide structure or capable of forming it on interaction with the lactam or its anion, eliminates the induction period and increases appreciably the rate of polymerisation of lactams (Fig. 1, curve *2*).

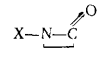
Thus, in the activated anionic polymerisation of lactams, the initial slow stage involving the nucleophilic addition of the lactam anion to the cyclic amide molecule is eliminated. In this case polymerisation begins immediately with rapid interaction of the activator molecules with the lactam anion, which is followed by the same intermediate reactions as in the non-activated polymerisation:



The scheme presented shows that the activated anionic polymerisation of lactams takes place as nucleophilic polyaddition of the lactam anion to the endocyclic carbonyl carbon atom of the imide, formed at the end of the growing macromolecule. One of the characteristic features of the anionic polymerisation of lactams is the absence of the elementary chain termination step. Theoretically, the stepwise addition of the lactam anion to the terminal imide group of the growing macromolecule can continue until the monomer is completely exhausted. However, as in polycondensation processes, this does not occur because of the influence of a number of physical and chemical factors, which include the following: the increase of the viscosity of the reaction medium, the attainment of equilibrium in the monomer–polymer system, and the decrease of catalytic activity. The change in the catalytic activity of the system during the anionic polymerisation of lactams is associated with numerous side reactions, which have been examined in detail in the excellent review by Šebenda[7].

III. CLASSIFICATION OF ACTIVATORS

It follows from the mechanism of the activated anionic polymerisation of cyclic amides examined above that the process activators are compounds having the general formula (I).



where X is an electron-accepting substituent. Evidently the activating capacity of compounds of this type will depend on the nature of the substituent at the nitrogen atom. Table 1 presents an estimate of the electrophilic properties of the substituents X capable of polarising the amide linkage within the ring. In analysing the data in Table 1, one should note that electron-accepting substituents function as a result of the presence of a positive charge on the key atom (Nos. 1 and 2) or in consequence of negative mesomeric and inductive effects (Nos. 3–9). When the

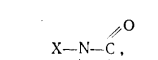
substituents are halogens (Nos. 10–13) or halogenoalkyl groups (No. 14), the strong $-I$ effect is partly compensated by a weak $+M$ effect. The combination of the two effects is reflected by the characteristic numerical Hammett (σ_n^*) and Taft (σ^*) constants.

Table 1. Estimated electrophilic properties of the substituents.

No.	Substituent R	Electronic formula	Conjugation effect	Dipole moment of C_6H_5R (Ref. 19)	σ_n^* substituent in aliphatic compound (Ref. 20)	σ_n (substituent in benzene ring) (Ref. 20)
1	$N(CH_3)_3$		$-I$; $-M$; $(+I_{CH_3})$	—	+0.859	1.90
2	NO_2		$-I$; $-M$	−4.03	+0.778	1.40
3	SO_2CH_3		$-I$; $-M$; $(+I_{CH_3})$	−4.44	+0.728	1.32
4	CN		$-I$; $-M$	−3.94	+0.628	1.30
5	$COCH_3$		$-I$; $-M$	−2.93	+0.516	0.60
6	$CO_2C_2H_5$		$-I$; $-M$; $(+I_{C_2H_5})$	−1.91	+0.522	0.71
7	COOH		$-I$; $-M$	—	+0.265	—
8	CHO		$-I$; $-M$	−2.75	+0.216	—
9	C_6H_5		$-I$; $-M$	—	+0.009	0.215
10	F		$-I$; $+M$	−1.57	+0.062	1.10
11	Cl		$-I$; $+M$	−1.57	+0.227	1.05
12	Br		$-I$; $+M$	−1.55	+0.232	1.00
13	I		$-I$; $+M$	−1.38	+0.276	0.85
14	CF_2		$-I$; $+M$	—	0.551	0.92

When the dipole moments are compared with the Hammett and Taft constants, one is bound to note a general tendency for all the electrophilic substituents listed in Table 1: an increase of the dipole moment corresponds to an increase of the constants σ_n^* and σ^*. The fact that, despite its large negative I effect, fluorine leads to a smaller value of σ_n^* than chlorine can be accounted for by its powerful $+M$ effect owing to conjugation with the benzene ring. The outer $2p$ orbitals of elements in the first Periods of the Periodic System are known[19] to be of approximately the same size as the π orbitals of double-bonded carbon. This leads to a more effective overlap of the orbitals than for heavier substituents (Cl, Br, and I).

It must be emphasised that the characteristics used to estimate the electrophilicity of substituents refer to substitution in aromatic and aliphatic series. However, the above tendency towards a change in the electrophilic properties of the substituents evidently persists also in the series of *N*-substituted lactams. Thus, it can be assumed

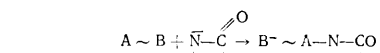
 (I)

that the whole series of compounds having the general formula (I) containing stronger electrophiles as *N*-substituents (Nos. 1–4 and 14) than the acyl group (No. 5), are effective, from the electronic standpoint, centres for the growth of macromolecules in the anionic polymerisation of lactams.

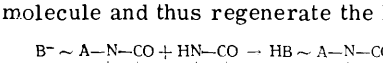
A wide series of both organic and inorganic compounds have been suggested as activators of the anionic polymerisation of lactams (see Table 2 below). Several attempts have been made at a classification of the activating compounds[6,21,22]. The influence of the geometrical and electronic structures of the above compounds on their activating capacity has been examined[8,22] and it has been suggested that activators be divided, on the basis of the nature of their action under the conditions of the anionic polymerisation of lactams, into "direct" activators, with an intrinsic activating capacity, and "indirect" activators, which interact with the lactam or its salt and form the activator.

According to Ikuzo et al.[22], activating compounds of the type A ~ B, where A and B are effective centres of the activator molecule, must meet the following requirements:

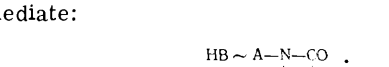
(1) A must be sufficiently electrophilic to combine with the lactam anion:



(2) The basicity of B must be sufficiently large to combine with a hydrogen atom linked to the nitrogen of the lactam molecule and thus regenerate the lactam anion:

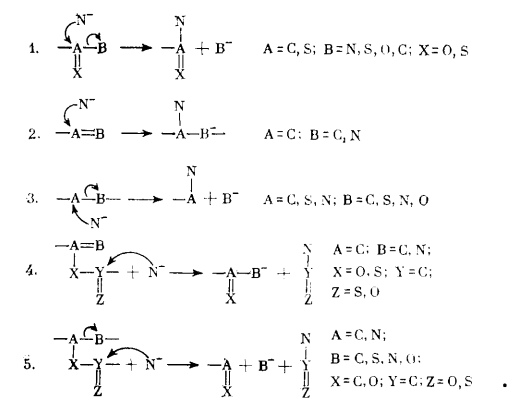


(3) A must assist in the cleavage of the C–N bond in the intermediate:



(4) The structure of A must be sterically favourable for attack by the lactam anion.

Compounds satisfying the above requirements have been divided into five types in accordance with their structure and the types of reactions leading to their formation[22]. The active centres of these compounds are shown schematically below:



The structures of many of the known types of activators (ethers and esters, *N*-alkylimides, lactaones, etc.) fit within the framework of the above requirements. In addition, Ikuzo et al.[22] tested the activating capacities of a number of other compounds, in particular a wide variety of triazine and pyridazine derivatives, azlactone derivatives, and other similar compounds. With some exceptions, the above compounds proved to be active under the conditions of the anionic polymerisation of lactams. On

Table 2. Classification of activating compounds.

No.	Class of compounds	Refs.	Suggested activation mechanism
1	(a) imides, carbamoyl-lactams, acyl-lactams	23—41	
	(b) isocyanates, isothiocyanates	42—49	$R-N=C=O+\bar{N}-CO \rightarrow R\bar{N}-CO-N-CO$
2	(a) carboxylic acid anhydrides and halides	50—58	$R-COX+\bar{N}-CO \rightarrow RCO-N-CO+\bar{X}$
	(b) halogenated linear and cyclic alkanones	59	$Cl-C-CO-C-Cl+\bar{N}-CO \rightarrow ClCCOC-N-CO+Cl^-$
	(c) organic peroxides	60	$Ar-COOOCO-Ar+\bar{N}-CO \rightarrow ArCOO-N-CO+\bar{O}CO-Ar$
3	(a) organic and inorganic acid esters	17, 60—80	$R-COO-R_1+\bar{N}-CO \rightarrow R-CO-N-CO+\bar{O}R_1$
	(b) lactones, thiolactones	81—90	$COO(CH_2)_n+\bar{N}-CO \rightarrow \bar{O}(CH_2)_n-CO-N-CO$
	(c) urethanes	91	$RNH-COOR_1+\bar{N}-CO \rightarrow RNHCO-N-CO+\bar{O}R_1$
4	(a) amides	92—99	$R-CONR_1R_2+\bar{N}-CO \rightarrow R-CO-N-CO+\bar{N}R_1R_2$
	(b) ureas, thioureas	100—103	$RNHCONHR+\bar{N}-CO \rightarrow RNHCO-N-CO+\bar{N}HR$
	(c) carbonylimidazoles	104, 105	$CH=CHN=CHNCOR+\bar{N}-CO \rightarrow RCO-N-CO+CH=CHN=CHN^-$
	(d) ketoamides	106—108	$RCORR_1R_2CONHR+\bar{N}-CO-\begin{cases}\rightarrow RCOCR_1R_2CO-N-CO+\bar{N}HR\\ \rightarrow RNHCO-N-CO+R_1R_2C=C(\bar{O})R\end{cases}$
	(e) diketones	109—112	$RCOCH_2COR_1+\bar{N}-CO \rightarrow RCO-N-CO+CH_2=C(\bar{O})R_1$
5	(a) nitriles, CN-lactams	113, 114	$R-C\equiv N+\bar{N}-CO \rightarrow RC(=\bar{N})-N-CO$ (или $N\equiv C-N-CO+R^-$)
	(b) CN-halides	115	$R-C\equiv N+\bar{N}-CO\begin{cases}\nearrow N\equiv C-N-CO+R^-\\ \searrow RC(=\bar{N})-N-CO\end{cases}$
	(c) dilactim ethers	116	$(CH_2)_xN=C-O-C=N(CH_2)_y+\bar{N}-CO \rightarrow \rightarrow(CH_2)_xN=C-N-CO+ O^-C=N(CH_2)_y \leftrightarrow OC-N^-(CH_2)_y$
	(d) cyanamides	104, 117	$NH_2-C\equiv N+\bar{N}-CO \rightarrow NH_2-C(=\bar{N})-N-CO$
	(e) carbodiimides, guanidines, imines, iminocarbonates	118—121	$ArN=C=NAr+\bar{N}-CO \rightarrow ArN=C(\bar{N}Ar)-N-CO$
	(f) azides	122	$R-N=N=N+\bar{N}-CO \rightarrow R-\bar{N}-N-CO+N_2$
	(g) triazines, pyridazines, pyrimidines, benzothiazoles	123—130	$N=CR-N=CR-N=CR+\bar{N}-CO \rightarrow N=CR-N=CR-\bar{N}=CR-N-CO$
6	(a) phosphonitrilic compounds $(PNX_2)_3$	131, 132	$N=PCl_2N=PCl_2N=PCl_2 \xrightarrow{+N-CO} N=PCl_2N=PCl_2N=PCl-N-CO+\bar{C}l$
	(b) alkylhalogenophosphines, alkyl halogenophosphites, phosphines, phosphates, phosphorus halides	133—138	$Ar-PX_2+\bar{N}-CO \rightarrow Ar-P(X)(N-CO)+X^-$; $ArPH_2+Na\bar{N}-CO \rightarrow ArP^+(H_2)(Na)\bar{N}-CO$
	(c) P_2O_5	139	$O=P-O-P(=O)-O+\bar{N}-CO \rightarrow O=P-N-CO+\bar{O}P(=O)_2$
7	oxides of Group VI elements, CO, CO_2, CS_2	140—149	$O=C=O+\bar{N}-CO \rightarrow O=C(\bar{O})-N-CO$

the basis of the results obtained, the authors concluded that there is a possibility of the specific synthesis of activators taking into account the above requirements.

However, one should note the difficulty of effecting the classification of activating compounds proposed by Ikuzo et al.[22]; by no means all activators can be described by

the proposed schematic equations (for example, cyanamides, CO, CO_2, sulphur and phosphorus halides and oxide halides, dilactim esters, diketones, etc.).

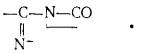
The classification of activating compounds proposed by Stehliček et al.[21] is based on their chemical structure:

(1) organic and inorganic acid esters and lactones;
(2) carboxylic acid anhydrides and halides;
(3) carboxylic acid amides, nitriles, and cyanamides;
(4) carbodiimides, isocyanates, isothiocyanates, ureas, urethanes, and guanides;
(5) derivatives of sulphonic and phosphoric acids;
(6) metal oxides and chlorides (Friedel–Crafts catalysts);
(7) other compounds such as fluoro-derivatives, organic peroxides, carbon disulphide, aromatic nitro-compounds, aliphatic polyhalides, etc.

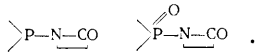
In this subdivision of indirect action activators compounds whose interaction with the lactam or its alkali metal salt leads to activating centres and side products (alcohols, acids, amines etc.) of different chemical types are included in a single class. For example, amides and nitriles, combined in a single class, interact with the lactam anion to form activating compounds having different chemical structures; the interaction of isocyanates with lactams does not lead to any side products, while urethanes, which belong to the same class according to Stehliček et al.[21], give rise to alcohols (Table 2).

We attempted to classify activators taking into account the chemical nature of the activating groups and side products formed. Table 2 includes activators of the anionic polymerisation of lactams taken from patent literature. All the compounds have been divided into seven classes, each class being further subdivided into subgroups in view of certain differences between the types of the active compounds formed within each class. Since it is impossible to specify unambiguously the mechanism of the formation of active centres, several versions of the proposed mechanism are quoted in many instances.

Compounds belonging to the first class are direct action activators, which form no side products poisoning the catalytic system and have therefore been considered separately. Compounds belonging to the second, third, and fourth classes form active centres with the same acyllactam structure. Despite this, these compounds have not been combined in a single class, since the side products formed differ in their chemical nature. Among compounds of the fifth class, the active species produced contains a group in which the nitrogen of the lactam ring is linked to an unsaturated system:



Characteristic side products are not formed for compounds of the fifth class. Phosphorus-containing compounds, forming active centres on interaction with the lactam or its anion, have been combined in the sixth class:

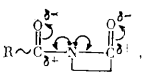


They give rise to acids as side products. The oxides of Group VI elements, CO, CO_2, and CS_2 have been assigned to the seventh class.

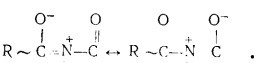
Thus, the classification which we propose for activators takes into account not only the nature of the active centre formed but also the nature of the side products, which have a significant influence on the rate of the anionic polymerisation of lactams. Thus alcohols, amines, acids, and other products arising on formation of the activating compounds lead to many side reactions, which poison the catalyst; among these, mention should be made of the decrease of the alkalinity of the system, the condensation of the aldehydes formed, the aminolysis of the reaction products, etc.

IV. THE INFLUENCE OF THE CHEMICAL STRUCTURE OF ACTIVATING COMPOUNDS ON THEIR EFFICIENCY

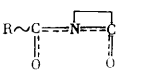
The influence of the chemical structure of activators on the rate of the anionic polymerisation of lactams has been considered in the literature mainly in relation to compounds of the acyl-lactam type. According to modern ideas[6,8–10], in the ground state of an *N*-substituted acyllactam the free electron pair of the nitrogen atom of the lactam ring can be involved in a resonance interaction with two neighbouring carbonyl double bonds (imide mesomerism),



which leads to the formation of two mesomeric forms:

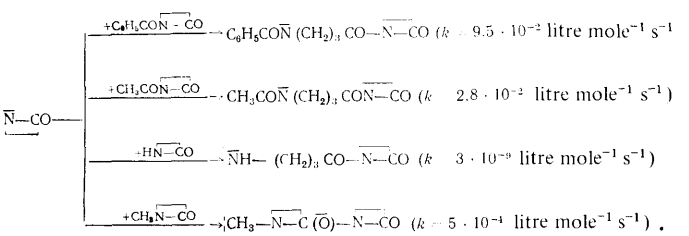


Such a resonance system can evidently be regarded as conjugated:



In the conjugated system the electron density in the endocyclic amide bond is reduced compared with a stabilised (also by resonance) lactam molecule. Evidently the electron-accepting properties of the group R tend to increase the polymerisation of the imide group in the direction of the electrophilic substituent, facilitating thereby the nucleophilic attack by the lactam anion on the increased positive charge of the endocyclic carbonyl group.

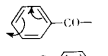
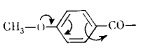
In order to elucidate the influence of the structure of a substituent at a nitrogen atom, measurements were made [150] of the rate of addition of pyrrolidinonatomagnesium bromide ($\dot{M}gBr^{-}\underline{N-CO}$) to *N*-substituted pyrrolidinones in tetrahydrofuran (THF) solution at 25 °C. The addition rate constants obtained are given below:



This method of estimating the activating capacity is in our view most correct, since it makes it possible to determine the differences in the influence of substituents in the very first stages of the interaction where the difference is most marked. Benzoylpyrrolidinone is more reactive than acetylpyrrolidinone, as can be seen from the addition rate

constants, which is probable due to the lower electronegativity of the acetyl group compared with the benzoyl group. For *N*-methylpyrrolidinone, one should expect a a lower value of k than that obtained, since the inductive effect of the CH_3 group acts in the opposite direction. However, the fact that in this instance the ring is not cleared constitutes, according to the authors[150], evidence demonstrating that compounds of this kind cannot be used as activators. The reaction of α-pyrrolidinone with its anion leads to polymerisation, despite the fact that the amine anion $H\overline{N}-(CH_2)_3CON-CO$ is not stabilised, as in the case of *N*-methylpyrrolidinone. The low addition rate constant explains the long induction periods in the non-activated polymerisation of lactams.

Table 3. Polymerisation of ϵ-caprolactam in the presence of *N*-acylcaprolactams as activators at 155°C.[151]*

Acyl group	Hardening time, s	Yield of polymer, %	Logarithmic viscosity, dl g^{-1}**
CH_3——→CO—	138	100	0.74
C_3H_7——→CO—	338	90.0	0.64
	625	81.6	0.65
	1520	18.3	0.52
$C_{16}H_{33}$—CO—	does not harden	4.5	0.25

*The percentage ratio of the activator and catalyst was 1.0:4.2.
**The viscosity was determined in a 0.5% H_2SO_4 solution at 25°C.

Scelis et al.[151] synthesised a number of *N*-acylcaprolactams, the acyl groups of which had different electronegativities (acetyl, butyryl, benzoyl, and *p*-methoxybenzoyl). The authors assumed that *N*-acyl-lactams having substituents with the most marked electron-accepting properties should exhibit the highest activity. However, the results (Table 3) showed that the size of the substituent has the dominant influence on the rate of the anionic polymerisation of lactams. The highest activity is manifested by *N*-acylcaprolactams with the smallest acyl groups. The effect associated with the electron-accepting properties of substituents is shown, according to authors[151], to a much smaller extent.

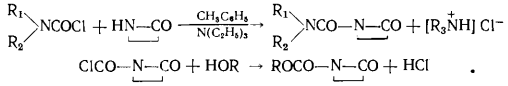
We believe that an estimate of the activating capacity on the basis of parameters such as the time of the onset of thickening, the degree of conversion, and the logarithmic viscosity of a dilute polymer solution is not altogether correct. It follows from the polymerisation mechanism that acyl groups exert the greatest influence on the reactivity of the carbonyl moiety of the imide group of the lactam in the first steps of the addition of the lactam anion.

Stehlíček et al.[152] investigated the influence of the structure of the acyl group on the rate of anionic polymerisation of ϵ-caprolactam by measuring the initial rate of polymerisation at a rigorously defined temperature (100° ± 0.2°C) and a concentration of the catalytic system of 0.2 mole %. The relative activating capacity was estimated from the time of the appearance of turbidity in the polymerising system and the following data were obtained for a number of *N*-acyl-lactams:

Group	CH_3	C_3H_7	C_4H_9	C_5H_{11}	C_6H_5	$CH_3OC_6H_4$
Time, min	13.8—14.5	14.3	17.2	14.7	14.1—16.3	16.5—17.2

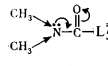
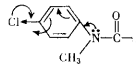
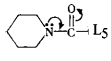
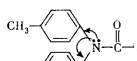
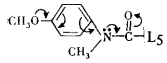
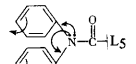
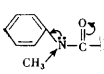
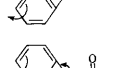
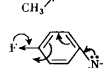
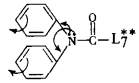
It was noted that anionic polymerisation activated by alkyl-imides obtained from aromatic carboxylic acids is much faster in the first seconds than in the presence of aliphatic acyl-lactams, but 30 s from the start of polymerisation the two rates become virtually equal.

Falkenstein and Dörfel[8] obtained disubstituted carbamoyl-lactams and esters of lactam-*N*-carboxylic acids via the mechanism



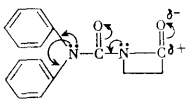
Examples of both classes of compounds proved to be effective activators of the anionic polymerisation of lactams at 120–150°C, and it was possible to vary the activating capacity of disubstituted carbamoyl-lactams and lactam-*N*-carboxylic acid esters within wide limits by the introduction of specific substituents. In order to estimate the efficiencies of the activators obtained, measurements were made of the time from the instant of mixing of the reagents to the onset of thickening and the results were compared with the basicity constants pK_b of the secondary amines used to obtain, *N*,*N*-disubstituted carbamoyl-lactams (Table 4).

Table 4. Dependence of the rate of polymerisation (thickening time) on the chemical structure of disubstituted carbamoyl-lactams[8].

Activator	Thickening time, min		pK_b for initial amine	Activator	Thickening time, min		pK_b for initial amine
	120°	150°			120°	150°	
	—	—	0.5		3.8	0.94	10.5
	—	—	0.9		1.85	0.5	13.4
	10	4.3	8.0		1.45	0.4	14.4
	7.8	2.5	9.1		1.1	0.2	14.4
	7.2	1.8	9.2		1.0	0.15	15

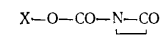
*L_5 = α-pyrrolidinone.
**L_7 = ϵ-caprolactam.

It follows from Table 4 that the activating effect of the compounds under consideration depends significantly on their chemical structure. Carbamoyl-lactams with aliphatic or alicyclic substituents at the exocyclic nitrogen atom (*N*,*N*-dimethyl, piperidinyl) do not activate the anionic polymerisation of lactams at all. The introduction of phenyl substituents leads to the appearance of an activating capacity in carbamoyl-lactams. This influence of the phenyl substituent is attributed [8] to the increase of the polarisation of the carbamoyl-lactam under the influence of the benzene ring in consequence of its negative inductive and mesomeric effects.

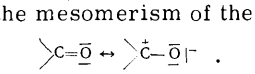


The rate of polymerisation depends both on the number of phenyl substituents and on the nature of the substituents in the benzene ring (if such are present).

In lactam-*N*-carboxylic acid ester



the activating effect diminishes with increase of the electronegativity of the substituent X (Table 5). It is believed [8] that the cause of this may be that the electronegative substituent X opposes the involvement of the polar structure in the mesomerism of the carbonyl group:



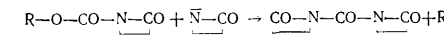
Thus the C...O bond order increases and the absorption band of the carbonyl group undergoes a bathochromic shift, as can be seen from Table 5. This corresponds to a decrease of the polymerisation of the amide bond in the lactam owing to the inductive effect, which leads to a weakening of the activating influence of the electronegative substituents.

Table 5. Dependence of the rate of polymerisation (thickening time) on the chemical structure of lactam-*N*-carboxylic acids [8].

Activator	Thickening time, min		ν_{CO}, cm^{-1}	Activator	Thickening time, min		ν_{CO}, cm^{-1}
	120°	150°			120°	150°	
ClC_6H_4—O—CO—L_5*	—	—	1726	$C_6H_5CH_2$—O—CO—L_5	1.25	0.25	1720
FC_6H_4—O—CO—L_5	—	—	1725	L_5CO—O—$(CH_2)_4$—O—COL_5	1.15	0.15	1710
$CH_3C_6H_4$—O—CO—L_5	—	—	1725	C_2H_5—O—CO—L_5	1.1	0.15	1717
C_3H_7—O—CO—L_5	1.5	0.5	1718	L_5CO—$O(CH_2)_6$—O—COL_5	1.1	0.1	1710
C_3H_7—O—CO—L_7**	1.4	0.3					
CH_2=CH—CH_2—O—COL_5	1.3	0.3	1720	L_7CO—$O(CH_2)_4$—O—CO—L_7	1.0	0.09	1708

*L_5 = ε-caprolactam.
**L_7 = η-caprinolactam.

Unfortunately Falkenstein and Dörfel [8] did not investigate the activating capacity of lactam-*N*-carboxylic acid esters as a function of the concentration of the catalyst; nor are data available about the isolation of any intermediates in the polymerisation process. The authors' explanation of the mechanism of the action of activators of this kind is therefore not sufficiently well founded. In all probability the activating effect of lactam-*N*-carboxylic acid esters should be sought in the possible interaction of the latter with the lactam or its anion (by analogy with carboxylic acid esters—see Table 2):



which leads to the exhaustion of the alkaline process catalyst. The acidity of the alcoholic residue will then play the main role in interaction with the process catalyst.

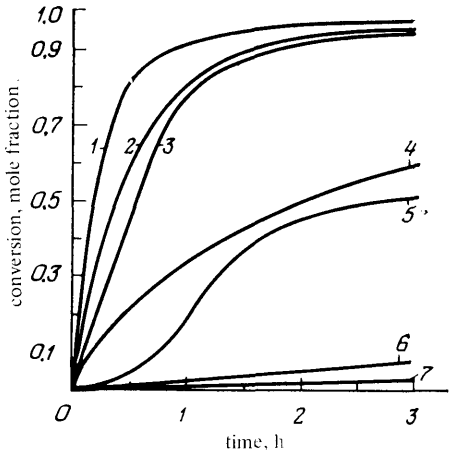
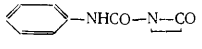


Figure 2. Time variation of the degree of conversion in the anionic polymerisation of ε-caprolactam at 130°C; [155] [NaH] = 0.0067 (mole fraction): 1) *N*-benzoyl-ε-caprolactam; 2) diisopropylcarbodiimide; 3) phenyl isocyanate; 4) *N*-acetyl-ε-caprolactam; 5) 1,3-diphenylurea; 6) 1,3-diethylurea; 7) n-butyl acetate.

Stehlíček et al. [21] showed in relation to a large class of compounds used as activators that, when the activating compounds interact with the lactam or its anion, the side products formed have an inhibiting influence on the rate of anionic polymerisation of lactams. Among the large number of compounds proposed as activators, only *N*-acyl-lactams and the products of the interaction of mono- and poly-functional isocyanates with lactams have therefore been widely used hitherto [153,154].

It is noteworthy that the conditions in the polymerisation of lactams have an appreciable influence on the nature of the action of activators of both direct and indirect types. A study [155] undertaken to estimate the relative activating capacities of various compounds used in the anionic polymerisation of lactams is of definite interest in this connection. Figs. 2 and 3 present kinetic curves for the variation of the degree of conversion with time in the presence of various activators of the anionic polymerisation of ε-caprolactam at 130° and 180°C. It is seen that the activating capacity of benzoylcaprolactam is higher than that of acetylcaprolactam, particularly at low polymerisation temperatures. The reaction of phenyl isocyanate with ε-caprolactam takes place with formation of phenyl-substituted carbamoyl-ε-caprolactam



by direct addition without the isolation of side products. Despite the intermediate stage, the initiation reaction is in this case (both at 130° and 180°C) appreciably faster than in the reaction involving acetylcaprolactam.

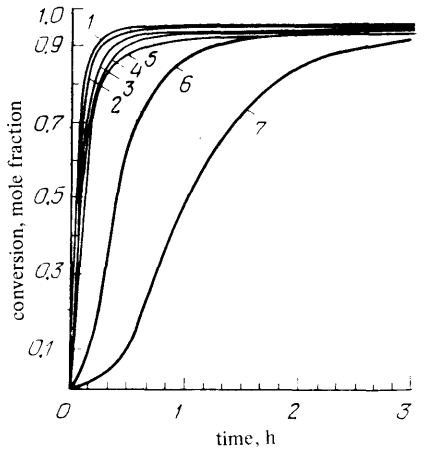


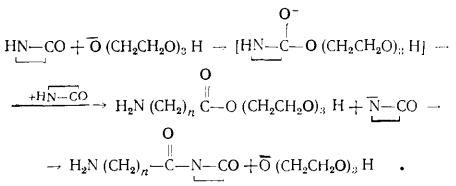
Figure 3. Time variation of the degree of conversion in the anionic polymerisation of ϵ-caprolactam at 180°C;[155] [NaH] = 0.0067 (mole fraction); mole fraction of activator 0.0067: 1) diisopropylcarbodiimide; 2) *N*-benzoyl-ϵ-caprolactam; 3) phenyl isocyanate; 4) *N*-acetyl-ϵ-caprolactam; 5) 1,3-diphenylurea; 6) 1,3-diethylurea; 7) n-butyl acetate.

sym-Ureas are known[21] to decompose at high temperatures to isocyanates and amines. The reduced effect of activators of this kind is determined by the basicity of the amined formed. In the case of aniline the free electron pair of the nitrogen atom is stabilised by the $-I$ and $-M$ effects of the benzene ring and the basicity of the amino-group is reduced. *sym*-Diphenylurea is therefore a more effective activator than 1,3-diethylurea, particularly at low polymerisation temperatures.

n-Butyl acetate gives rise to a longer induction period both at 130° and at 180°C. However, at the higher polymerisation temperature in the presence of n-butyl acetate it is possible to attain a high degree of conversion, comparable with the values obtained in the presence of *N*-acetyl-ϵ-caprolactam. When the n-butyl group is replaced by the t-butyl, phenyl, or isopropyl group, the activating capacity of the ester increases[21].

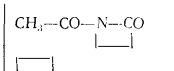
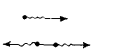
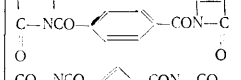
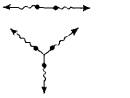
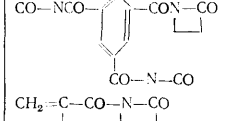
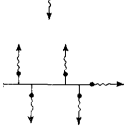
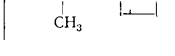
According to Stea and Gechell[155], diisopropylcarbodiimide has a high activating capacity over the entire temperature range. Its activating influence can be accounted for in two ways: by the interaction of the carbodiimide with an acid hydrogen atom (traces of water), leading to the formation of *sym*-dialkylureas[156], or by the addition to the carbodiimide of the lactam or its anion with formation of a polar substituent at the lactam nitrogen[21].

The fact that alcohols, which were usually regarded as inhibitors of the polymerisation of lactams, behave at the same time as its activators is of special interest. The use of alcohols as activators of the anionic polymerisation of lactams was first reported by Čefelin et al.[157] and then Mermoud[158] used triethylene glycol as the activator and obtained a product with a high degree of polymerisation. The problem of the use of alcohols for the activation of the polymerisation of lactams was investigated in detail by Sekiguchi[159]. His results show that activation under the influence of alcoholic hydroxyl is due to the imide groups formed as a result of the esterification (decyclisation) of the lactam molecules:



Sekiguchi[6] established experimentally that the activating capacity of alcohols depends to a large extent on the acidity of the alcoholic hydroxyl. Apart from triethylene glycol, an activating capacity is shown, according to his data, by diethylene glycol, 1-octanol, tetradecanol, s- and t-butyl alcohols, etc. We believe that, on the basis of Sekiguchi's mechanism of activation, alcohols should be regarded as catalysts of the anionic polymerisation of lactams, since the growing polyamide chain does not contain an alcoholic radical.

Table 6. The direction of the growth of macromolecular chains in the anionic polymerisation of ϵ-caprolactam in the presence of mono- and poly-functional activators[167].

Activator	Structural formula	Functionality	Schematic illustration of the direction of the macromolecular chain growth
N-Acetyl-ϵ-caprolactam		1	
N,N'-Isophthaloyl-bis-ϵ-caprolactam		2	
N,N',N''-Trimesoyl-tris-ϵ-caprolactam		3	
N-Methacryloyl-ϵ-caprolactam		>3	

V. THE INFLUENCE OF THE FUNCTIONALITY OF ACTIVATORS ON THE MOLECULAR STRUCTURE OF THE POLYMERS FORMED

The activators of the anionic polymerisation of lactams not only accelerate the polymerisation process but also constitute an effective means for the specific regulation of the molecular structure and hence of the properties of the polyamides formed[34,35,160–166].

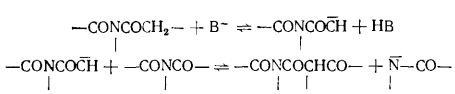
The majority of the activators considered above contain one functional group which ensures the activation and growth of the polymer chain in one direction and this leads to the formation of polymers having a predominantly linear structure. The use in the polymerisation of lactams of

polyfunctional activators, i.e. compounds containing several activating functional groups in their molecule, leads to the formation of polyamides of "star" or "comb" type[165,167]. Thus the direction of growth and the number of growing chains of the macromolecules are related to the disposition and number of the functional groups in the activator molecule. This is illustrated schematically in Table 6.

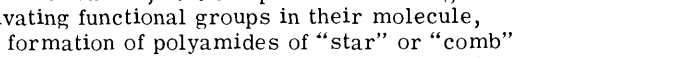
However, one should note that the polyamides obtained in the presence of monofunctional activators are not linear polymers in the strict sense of the term. It is known[165, 168-171] that the synthesis of polyamides is accompanied by side reactions leading to the formation of polymers with a low degree of branching. The degree of branching of these polyamides is determined in the study of their molecular weight distribution[165,168,169] and from end group analysis[170,171]. It was shown that the number of end groups in the polyamide macromolecules formed in the presence of a monofunctional activator is greater than two[170,171] and that the molecular weight distribution in such polyamides is broad owing to branching reactions occurring at late stages of the process[165,168,169].

The molecular structure of the polyamides obtained in the presence of polyfunctional activators is more complex. In this case the branching of the polyamides is caused, on the one hand, by the functionality of the activator (Table 6) and, on the other, it is due to the same side reactions which occur also in the formation of polyamides in the presence of monofunctional activators. In the presence of polyfunctional activators the products are polyamides containing, apart from soluble macromolecules, also insoluble macromolecules[34,35,161-166], which is associated with the three-dimensional structure of the latter[165,166,172]. In a study of the molecular structure of soluble specimens of polycaproamide in the initial stages of the polymerisation (up to the instant of gel formation) Pavlova showed[165] that the test specimens contain two groups of fractions—with higher and lower degrees of branching. The molecular weight distribution obtained by Pavlova et al.[165] from fractionation data revealed the presence of two maxima corresponding to narrow and broad distributions. The narrow distribution was explained by the presence in the polyamide chain of macromolecules with non-random branching due to the polyfunctionality of the activator, while the broad distribution was attributed to the presence of macromolecules with random branching[165]. The presence of the above two molecular structures in the polyamides formed—with random and nonrandom branching—can probably be explained by the occurrence of side reactions during the formation of the polyamides.

The reactions which can lead to branching under the conditions of the activated polymerisation of lactams can probably also lead to the formation of cross-linked macromolecules. Wichterle[173] and Šebenda[174] showed in model reactions that in an alkaline medium the imide groups of the compounds undergo the Claisen condensation when the α-carbon atom in the molecule is linked to at least one hydrogen atom:

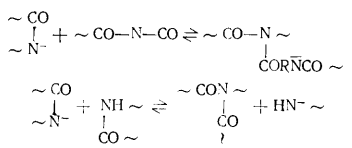


The *N*-acylated β-ketoacid amides (ketoimides), formed as a result of the above reaction, can react with the growing acyl-lactam centres and can lead to the formation of ketoimides of various structures[175,176]. When cyclic ketoimides interact with the lactam anion, they can be converted into ketoamides[176]:



Both ketoamides and ketoimides, containing reactive groups ($>C=O$, $-CH_2-$, $-\underset{|}{C}H-$) can lead to a large number of different compounds under the conditions of the anionic polymerisation of lactams, particularly to hydroxypyridine and uracil derivatives[173], which can serve in their turn as centres for branching and cross-linking in the polymers produced.

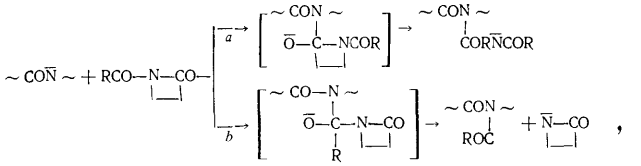
Wichterle and coworkers[177,178] and Šebenda[7] suggested that the branching of macromolecules in the anionic polymerisation of lactams can be caused by reactions of the type



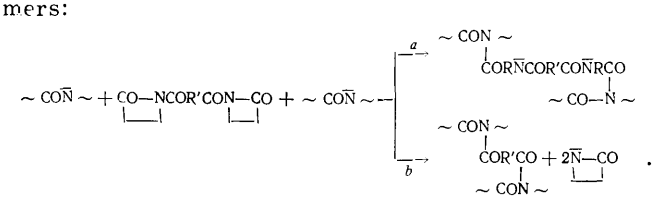
in addition to the side reactions mentioned above.

The above results indicate the possibility of branching and cross-linking in polyamides when the anionic polymerisation of lactams is carried out in the presence of monofunctional and polyfunctional activators. However, when the polymerisation of ϵ-caprolactam was performed in the presence of monofunctional activators (with different proportions of the components of the catalytic systems and at different concentrations) the formation of insoluble polyamides was not observed. Thus the above literature data do not fully explain the cause of the formation of cross-linked polyamides in the presence of polyfunctional activators.

Frunze et al.[172] relate the cause of the formation of cross-linked polyamides to the presence in the growing polyamide macromolecules of terminal acyl-lactam groups capable of reacting with the amide groups of other macromolecules. They showed, for the model reaction of a polyamide (G-669) with mono- and poly-functional activators, simulating the reactive end-groups of the growing polyamide chains, that the reactions of the polyamide with monofunctional activators lead to the formation of *N*-substituted polyamides only:



while the reactions of the polyamide with bifunctional activators result in the formation of cross-linked polymers:



It was shown later[175] that pathways *a* and *b* of the above reactions depend to a large extent on temperature.

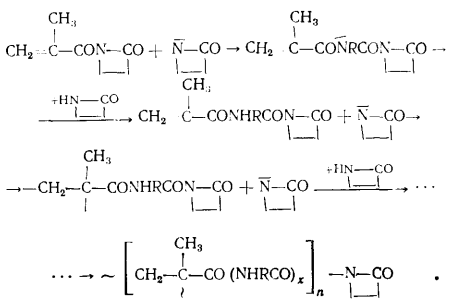
The literature data concerning the study of the molecular structures of polyamides, which were examined above, permit the conclusion that in the presence of monofunctional activators the products are linear polyamides with a low degree of branching, while in the presence of polyfunctional activators partially cross-linked polyamides with random branching are formed, the degree of branching increasing with increasing functionality of the activators [165].

N,*N*'-Acylbislactam (*N*,*N*'-isophthaloyl-, *N*,*N*'-terephthaloyl-, *N*,*N*'-adipoyl-, and *N*,*N*'-sebacoyl-biscaprolactams) were first used as bifunctional activators by Korshal et al. [160] in the anionic polymerisation of ε-caprolactam. They established that, depending on the concentration of the catalytic system, soluble or insoluble polyamides are formed and that, when a mixture of the above acylbislactams with a monofunctional activator in different proportions is used, it is possible to regulate fairly readily the molecular weight of the polymers produced [60]. *N*,*N*'-Diacylbislactams have now found extensive applications in the activation of the anionic polymerisation of lactams [32, 100, 114]. Diisocyanates [35-47, 164, 180], in the presence of which soluble polyamides with a high strength are formed, are widely used as bifunctional activators.

N,*N*',*N*''-Trimesoylter-ε-caprolactam, in the presence of which polyamides with randomly branched and partly cross-linked structures are formed, was used for the first time as a trifunctional activator for the polymerisation of ε-caprolactam [35, 161]. It was shown [161] that the polyamides obtained in the presence of the trifunctional activator are more elastic and have a higher impact strength than the polyamides obtained in the presence of a monofunctional activator.

Muller [181] suggested that cyanuric chloride be used as an activator of the anionic polymerisation of α-pyrrolidinone. According to the author, three chlorine atoms in cyanuric chloride are substituted by α-pyrrolidinone and the resulting triazine derivative of α-pyrrolidinone act as an effective trifunctional activator of the anionic polymerisation of the lactam.

The use of acyl-lactams containing unsaturated groups as activators of the anionic polymerisation of lactams is of great interest. Such activators include *N*-methacryloyl-ε-caprolactam [34, 162, 163]. Formally, *N*-methacryloyl-ε-caprolactam can be classified as a monofunctional activator, since its molecule contains only one imide functional group. However, the polyfunctional nature of this activator is manifested in the course of the polymerisation of lactams, as can be seen from the polymerisation mechanism [162, 163]:



It is noteworthy that *N*-methacryloyl-ε-caprolactam does not polymerise in the process involving the double bonds via either a radical or an ionic mechanism [182]. The adduct *N*-methacryloyl-(ε-aminocapryloyl)-ε-caprolactam, formed as a result of the first step in the polymerisation of ε-caprolactam, polymerises via the double bonds, which leads to the formation of a polyfunctional activator [162, 163, 183].

As in the presence of the trifunctional activator *N*,*N*',*N*''-trimesoylter-ε-caprolactam, in the presence of *N*-methacryloyl-ε-caprolactam the products are insoluble polyamides which are randomly branched and partly cross-linked polymers with high strength. Table 7 shows that the physicomechanical properties of the polyamides depend on the functionality of the activator used. The impact strength of the polyamides synthesised using polyfunctional activators is much higher than that of the polymers obtained with *N*-acetyl-ε-caprolactam.

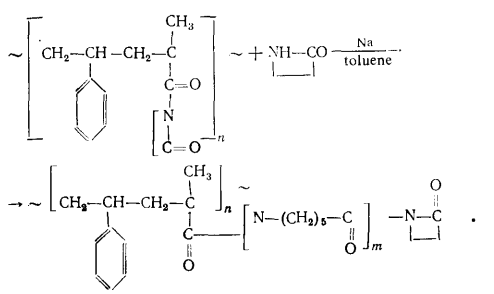
Table 7. Certain physicomechanical characteristics of polycaproamide obtained in the presence of activators with different functionalities relative to lithium Kapron B [162, 163, 184]

Activator	Content of fraction insoluble in HCOOH, wt.%	Ultimate strength, kgf cm^{-2}		Specific impact strength, kgf cm^{-2}
		on static bending	on compression	
N-Acetyl-ε-caprolactam	0	1300—1500	1100	100—150
N,*N*'-Isophthaloylbis-ε-caprolactam	0	1200—1400	1100	250—350
N,*N*',*N*''-Trimesinoylter-ε-caprolactam	60—70	1200—1400	1000	does not break
	40—50	1400—1500	—	does not break
N-Methacryloyl-ε-caprolactam	0	900	—	150—170
Kapron B				

Thus the data examined above permit the conclusion that the functionality of the activators has a significant influence on the molecular structure and properties of the polymers formed.

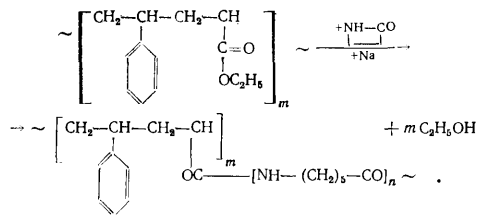
VI. MACROMOLECULAR ACTIVATORS OF THE ANIONIC POLYMERISATION OF LACTAMS

The use of polymeric molecules of different chemical types, containing acyl-lactam, isocyanato-, acid chloride, cyano-, and certain other functional groups, as activators of the anionic polymerisation of lactams leads to the formation of graft and block copolymers. This leads to the possibility of a specific regulation of the properties of the polymeric materials formed. Depending on the positions of the activating groups in the macromolecular chain of the activator, graft or block copolymers are produced. Thus Wichterle and Gregor [182] grafted ε-caprolactam to a copolymer of styrene and *N*-methacryloyl-ε-caprolactam containing acyl-lactam groups:



Korshak and coworkers[185-188] developed a method for the copolymerisation of styrene with ε-caprolactam in bulk to aid the chemical moulding of large articles. According to this method, in the first stage styrene undergoes radical copolymerisation with catalytic amounts of *N*-methacryloyl-ε-caprolactam in solution in ε-caprolactam. In the second stage ε-caprolactam is grafted to the macromolecular activator formed in the reaction mixture. The authors showed that an increase of the content of polystyrene units in the copolymer greatly increases the water resistance of the material but its strength (particularly the specific impact strength) decreases.

Graft copolymers have been obtained[189] by the anionic polymerisation of ε-caprolactam in the presence of a copolymer of styrene with ethyl acrylate, the ester group of which activates the polymerisation of the cyclic amide:



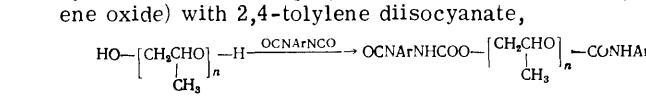
If the styrene–ethyl acrylate copolymer contains more than 1 wt.% of ethyl acrylate, a cross-linked insoluble product is formed, which the authors[190] explain by the presence of a tertiary carbon atom in the α-position relative to the ester group.

The grafting of α-pyrrolidinone[191] and ε-caprolactam[192] to poly(acryloylchloride) has been described:

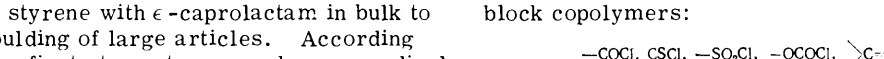
It was noted that fibres and films with a high strength can be obtained from the graft copolymers of acrylic acid with ε-caprolactam and α-pyrrolidinone thus synthesised.

The use of acyl-lactam, acid chloride, isocyanato-, and other groups at the ends of macromolecules of different chemical type for the activation of the polymerisation of lactams in order to obtain block copolymers is known. In this case block copolymers with the structure A–B–A, in which the two outer segments A are polyamide units and the inner segment B is some other polymer, are as a rule obtained. The molecular weight of the inner segments and the ratio of the macromolecular activator and the lactam giving rise to the polyamide units of the outer segments vary within wide limits, which makes it possible to vary also the properties of the block copolymers. The use of polyethers and polyesters[193-196], polythioethers[196], polycarbonates[196], polybutadienes[197-199], polystyrene[197, 200-202], polysulphone[203], and polyamides of other chemical types[204-207] as the inner segments of block copolymers has been reported.

For example, a method has been described for the synthesis of block copolymers[196] by treating poly(propylene oxide) with 2,4-tolylene diisocyanate,

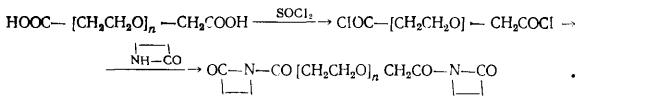


and subsequent polymerisation of ε-caprolactam in the presence of the resulting polymeric activator. It has been pointed out[196] that, apart from polyesters and polyethers, polythioethers, polyamides, and polycarbonates containing the following terminal functional groups can be used as the internal polymeric segment in the synthesis of block copolymers:



ε-caprolactam, ξ-oenantholactam, η-caprinolactam, ω-dodecylactam, and their *C*-substituted derivatives have been used as the lactam components.

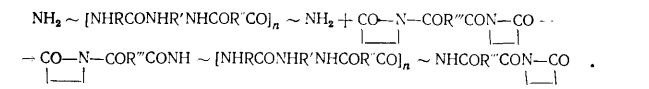
According to another procedure[193], the terminal carboxy-groups of poly(ethylene glycol) are initially converted into acyl chloride groups by reaction with thionyl chloride in solution in xylene and then into acyl-lactam groups as a result of reaction with ε-caprolactam in the presence of pyridine:



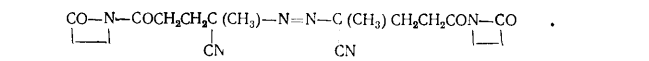
The compound obtained is used as a macromolecular activator of the anionic polymerisation of ε-caprolactam. The block copolymer formed has antistatic properties which are improved compared with those of polycaproamide.

Jamashita et al.[194] used poly(tetramethylene glycol) with terminal chloroformate groups, obtained by treating the terminal hydroxy-groups with phosgene, as the polymeric activator of the anionic polymerisation of α-pyrrolidinone and ε-caprolactam. As polymerisation proceeds in the presence of the above polymeric activator, the authors observed an increase in the degree of conversion of the lactam and an increase of the intrinsic viscosity of the block copolymer formed. A linear relation was observed between the logarithm of the intrinsic viscosity and the logarithm of the degree of conversion of the lactam, which indicates, according to the authors[194], the absence of a chain termination reaction. The comparatively low concentration of the polymeric activator (2–4%) indicates a fairly high efficiency of poly(tetramethylene glycol) bischloroformate as an activator of the polymerisation of lactams.

Lincoln[204] used the reaction of the terminal amino-groups of the mixed polyamide 6/66 with *N*,*N*′-acylbislactam in order to obtain a polymeric activator for the synthesis of a block polyamide:



Polystyrene with terminal *N*-acylpyrrolidinone groups[201], synthesised by the radical polymerisation of styrene using 4,4′-azobis(pyrrolidinono-4-cyanovalerate) as the initiator, proved to be an effective activator of the polymerisation of α-pyrrolidinone:



The linear increase of molecular weight with increasing degree of polymerisation of α-pyrrolidinone as well as the increase in the degree of conversion and of the intrinsic viscosity with time confirmed, according to the authors[201], the stepwise chain propagation and the absence of chain termination during polymerisation. The authors do not quote any information about the activation of the anionic polymerisation of the lactam involving the inner –C≡N groups of the macromolecular activator.

Korshak and coworkers [205,206] described the synthesis of block copolymers involving the interaction of an N,N'-acylbislactam with a diamine in an ϵ-caprolactam melt,

$$(n+1)\ \underset{\underset{|__|}{}}{\mathrm{CO{-}NCOC_6H_4CON{-}CO}} + n\ \mathrm{NH_2R'NH_2} \rightarrow$$

$$\rightarrow \underset{\underset{|__|}{}}{\mathrm{CO{-}NCOC_6H_4CO{-}}}\ [\mathrm{NHR'NHCOC_6H_4CO}]_n\ \underset{\underset{|__|}{}}{\mathrm{{-}N{-}CO}} + 2n\ \underset{\underset{|__|}{}}{\mathrm{NH{-}CO}},$$

with subsequent sodium-catalysed polymerisation of ϵ-caprolactam via the terminal acyl-lactam groups of the resulting polymeric activator. It was established that, with increase of the content of the polymeric activator in the reaction mixture, the degree of conversion of ϵ-caprolactam increases and the thickening time diminishes, which indicates an increase of the rate of polymerisation. When the ratio of the initial polymers is altered, block copolymers of the type A–B–A with different lengths of the segments are formed; this is also indicated by a change in the intrinsic viscosity and melting point of the resulting copolymers.

Very interesting and very promising studies have been made on the synthesis by anionic polymerisation of block copolymers of polybutadiene, containing terminal isocyanato-groups, with a lactam [197-199]. The presence of unsaturated double bonds in the butadiene segment,

$$\sim [\mathrm{CO(CH_2)_5\ NH}]_m\ \mathrm{{-}CONH{-}}\ [\mathrm{CH_2CH{=}CH{-}CH_2}]_n\ \mathrm{{-}NHCO{-}}\ [\mathrm{NH(CH_2)_5\ CO}]_m \sim$$

leads to further possibilities for the modification of the products. The authors [197] note the exceptionally high elasticity of the butadiene block copolymers even when the content of the ϵ-caprolactam units is up to 70–80%. It was shown that the plasticity of this polymer depends on the molecular weight of the polycaproamide segments. The high degree of conversion (~98% with respect to ϵ-caprolactam) shows that the macromolecular butadiene activator is highly effective. The impact strength, determined for hardened block copolymers with the above structure, increases with increasing content of the lactam units and increases sharply when the latter is more than 50%, which the authors [198] attribute to the higher impact strength of polycaproamide compared with the hardened polybutadiene. At the same time, the bending strength changes insignificantly with increasing fraction of polycaproamide in the block copolymer.

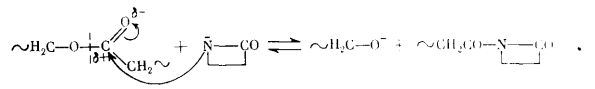
Thus the data presented concerning the use of macromolecular activators in the anionic polymerisation of lactams permit the following conclusions.

1. Prepolymers containing the $-O-$, $-COO-$, $-COCl$, $-CSCl$, $-SO_2Cl$, $-OCOCl$, $\rangle C{=}C{=}O$, $-N{=}C{=}O$, $-\underset{\underset{|__|}{}}{\mathrm{CON{-}CO}}$, etc. functional groups are effective activators of the anionic polymerisation of lactams.

2. The activating capacity of compounds of this kind is determined mainly by the nature of the functional group and not the length and nature of the macromolecular chain.

3. The properties of graft and block copolymers depend both on the activator : lactam ratio and on the nature of the macromolecular chain of the polymeric activator.

The anionic polymerisation of lactams can be activated not only by the functional groups at the ends of the macromolecules but also by the functional groups which are fragments of the main polymer chain. Thus it has been reported [207,208] that polyesters and polyethers can be used as activators of the anionic polymerisation of lactams. As a result of nucleophilic attack by the anion of the ester group, the heterobond is dissociated with chain transfer to the lactam molecule:



This case constitutes an example of chain transfer reactions with dissociation, which are common in the polymerisation of heterochain monomers [209]. As the interchain exchange reactions proceed, the block copolymers formed at the beginning of the process can be converted into a statistical polymer. For example, Korshak and Frunze [210] established that, when a mixture of homopolyamides is heated, a block copolymer is formed initially; the interchain exchange reactions gradually reduce the size of the blocks and the system attains a state of equilibrium characterised by the most probable distribution of the monomeric units in the copolymer.

It has been noted [206] that, when the anionic polymerisation of ϵ-caprolactam is carried out in the presence of polyhexamethyleneisophthalamide with terminal N-acyllactam groups at 140° and 180°C, the products are block copolymers whose intrinsic viscosities differ appreciably [η_{int} (140°) > η_{int} (180°)]. The authors explain the difference between the viscosity characteristics [206] by the fact that at 140°C the exchange reactions leading to interchain exchange and ultimately to the formation of block copolymers with a less regular structure proceed much more slowly than in the polymerisation at 180°C.

Taking into account the set of the possible exchange reactions in the anionic polymerisation of lactams in the presence of macromolecular activators, one must bear in mind that in practice one cannot obtain a "pure" block copolymer of the type A–B–A. In reality, under the influence of the interchain exchange, the system may contain, together with the block copolymer formed, also a graft copolymer and a mixture of homopolymers. The chemical structure of the products will be determined in each specific instance by the process conditions, i.e. by the nature of the macromolecular activators and the lactam, their proportions, temperature, reaction time, etc.

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Analysis of Atmospheric Pollutants by Gas Chromatography

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Chromatographic methods for the analysis of atmospheric pollutants, including the principal stages of the determination, from the sampling procedure to the evaluation of the results of the analysis, have been examined. The difficulties and limitations frequently encountered in the examination of the separate stages of the analysis and the various methods have been analysed. The review is based on work published in the period 1965-1978. The bibliography contains 398 references.

CONTENTS

I.	Introduction	1006
II.	Air sampling procedure	1006
III.	Detectors. Calibration	1010
IV.	Characteristic features of the qualitative and quantitative analysis of micro-quantities of harmful substances in air	1012
V.	Analysis of inorganic substances	1013
VI.	Analysis of organic substances	1015
VII.	Summary	1017

I. INTRODUCTION

The contamination of the environment, particularly the atmosphere, which in many countries has become a serious international problem, is posing analytical chemistry important and complex problems in the analysis of many-component mixtures of various atmospheric pollutants, the components of which are present in trace concentrations. Practically the whole arsenal of physical and chemical methods available to analytical chemistry is now being used for the analysis of atmospheric pollutants [1]. Its high sensitivity and extremely high selectivity have made gas chromatography one of the basic methods of analysis in the chemistry of industrial hygiene and the chemistry of the atmosphere.

The importance of the problem of analysing the atmosphere is to a large extent responsible for the large number of publications on this subject, and the number is increasing continuously [2,3]. In 1968, a detailed review [4] analysed the achievements of gas chromatography during ten years of application in the chemistry of the atmosphere. A number of later reviews and monographs deal with the gas-chromatographic analysis of atmospheric pollutants [5,6] and the chromatographic determination of harmful substances in the air of industrial plants (industrial atmosphere). [7] The present review includes material published in the period from 1965 to 1978.

At the present time, the problem of separating complex mixtures of substances by gas chromatography often presents no special difficulties. The use of stationary phases of high selectivity (particularly in micro-packed capillary columns) and capillary columns with a separation efficiency of > 200000 theoretical plates makes it possible to separate and analyse complex mixtures of organic and inorganic compounds consisting of several hundred components. Another important advantage of this method is its extremely high sensitivity, which makes it possible to determine micro-concentrations of a substance at a level of 10^{-10}%†.

Nevertheless, the gas-chromatographic method also encounters certain difficulties in the analysis of micro-quantities of various toxic substances in air. Since the maximum permissible concentrations (MPC) for most toxic chemical compounds in the air of industrial plants is 0.01-0.001 mg m^{-3}, that is about 10^{-7}-10^{-8}%, the specimen of air for analysis, with a volume of 1-10 ml, should contain not more than 10^{-10}-10^{-12} g of the substance. This quantity lies at the limits of many chromatographic detectors used for the analysis of air [8]. The MPC of harmful substances in atmospheric air is lower by a factor of approximately 10. If in addition account is taken of the losses of the substance being analysed during sampling, the treatment of the sample and its introduction into the chromatograph, and the chromatographic separation, the problem of inadequate analytical sensitivity becomes particularly acute.

Another important problem is the qualitative analysis of many-component mixtures, since polluted air generally contains complex mixtures of chemical con pounds of different classes. The chromatographic analysis is also complicated considerably by rapid change in the composition of the air being analysed (particularly atmospheric air) under the influence of meteorological conditions and photochemical reactions taking place in the atmosphere between compounds present in the air, under the influence of solar radiation.

The gas-chromatographic analysis of micro-quantities of substances includes the following stages.

1. Sampling. Storage of the sample.
2. Concentrating the components.
3. Treatment of the sample and its introduction into the chromatograph.
4. Chromatographic separation of the components of the sample.
5. Detection, and also, at intervals,
   a) calibration of the chromatograph (detector);
   b) qualitative and quantitative analysis of micro-quantities of substances.

II. AIR SAMPLING PROCEDURE

Sampling (and the concentrating of micro-quantities of substances) presents one of the principal problems in the analysis of polluted air, because of the insufficient sensitivity of detectors and the existence of active sites, capable

†Here and subsequently, concentrations are given in wt.%.

of sorbing traces of material in the chromatographic apparatus (chromatograph connections, columns) and in the sorbents used. Concentrating the sample with micro-component concentrations at a level of 10^{-4}–10^{-5}% is often also carried out in work with highly sensitive ionisation detectors. In these cases it is usually sufficient to concentrate the components from one litre of the air being analysed. This technique is also used when it is impossible to carry out the direct analysis of the gaseous sample on capillary columns and in certain other cases.

Existing methods for sampling air can be divided into four groups: 1) sampling into various containers; 2) aspiration of the air through a solvent which retains the impurities; 3) absorption of harmful substances from the air by sorbents; and 4) freezing the impurities in a cooled trap on an inert packing or sorbent. The methods of the last three groups are techniques for concentration.

The simplest method is the direct introduction of the sample into the chromatograph. In this case the air is sampled with a glass or plastic syringe, and also into gas pipettes, steel or glass bottles, bags made of polymer film, and other containers. With this method, satisfactory results are obtained only in the analysis of gaseous samples containing traces of substances which are not too polar (light hydrocarbons, oxides of carbon, nitrous oxide, etc.). The accuracy of these determinations is low because in practice it is very difficult to take account of the losses of the substances being analysed, which in some cases (the analysis of reactive gases and vapours) may reach 40%[9]. Not only reactive compounds, but also hydrocarbons, are adsorbed on the walls of containers[4].

The sampling of components for analysis by absorption in a suitable solvent is also a method for the equilibrium concentrating of these compounds. In contrast to the case of sampling into containers, there is practically no limit to the range of substances that can be analysed by this method. In addition, the aspiration of the sample through a solvent makes possible the selective removal of substances of different classes from the air. Nevertheless, sampling into a solvent is not often used in chromatographic analysis, since it is not possible to achieve a very high sensitivity in the determination. This is because, despite the high degree of enrichment of the substances of the sample in the solution being analysed, only a small fraction of the absorbing liquid is taken for analysis (1–10 μl), that is 0.1–0.2% of the original volume of the solution, which should not be less than 3–5 ml. It is true that the sensitivity can be increased by repeating the concentration procedure, for example by evaporating the solution after sampling. This introduces an additional error into the determination, however, due to the volatility of the dissolved compounds of the sample. To avoid possible errors in the analysis of trace quantities, it is also necessary to take account of the volatility of the solvent itself and the rate of aspiration of the air through the absorber. To increase the sensitivity it may be more promising to extract the substances dissolved in the absorbing liquid by a much smaller volume of a selective solvent, that is by a repeated concentration. This is because the extracting agents used are solvents for which the distribution coefficient of the trace component is much greater than that of the main component[10].

A method particularly widely used in the gas-chromatographic analysis of atmospheric pollutants is frontal non-equilibrium concentration, based on the complete absorption of heavy impurities by sorbents with a highly developed surface. The substances being analysed are collected in traps (columns) filled with a small quantity of sorbent (silica gel, active carbon, polymeric sorbents)[4,11]. These are then desorbed and separated in a chromatographic column. The calculation of the minimum length of the trap, that is the length in which all the heavy trace components being analysed are completely retained, has been described in a monograph[10]; the equations given make it possible to formulate the principal requirements to be satisfied by the parameters of the concentration process and to carry out different versions of the analysis. An advantage of the frontal method of concentration is that it is possible to absorb large quantities of trace components quantitatively from the air (high degree of enrichment). In addition, sampling is usually carried out at the temperature of the surrounding medium (rarely with cooling). Moisture does not interfere in the determination for most sorbents (active carbon, graphitised carbon black, Porapak-S), since these sorbents are hydrophobic. By concentrating the substances in the sample on adsorbents, it is possible to achieve a very high sensitivity of the determination; it is often not necessary to pass large volumes of air through the trap, particularly when a sensitive detector is used. In this case the trap acts as a sampler rather than a concentrator.

A disadvantage of the frontal method of concentrating trace quantities is the difficulty of desorbing the substances absorbed by the trap, particularly when the trap is heated (that is in thermal desorption). A high desorption temperature for the trace components may lead to various undesirable side reactions, for example in the determination of unstable compounds. It is often therefore preferable to use displacement (extraction) of the trace components by a suitable solvent[10].

An adsorbent used particularly frequently in the frontal concentration of trace components is active carbon, which at a temperature from −60°C to +20°C can be used successfully for sampling and concentrating pollutants in atmospheric[4] and industrial[12] air. It should be noted that a concentrator containing active carbon has a very high adsorption capacity and retains micro-components strongly, making their thermal desorption difficult. Moreover, carbon reacts with various sulphur-containing compounds, and to trap effectively substances with a low molecular weight (ethylene, methylene chloride), extensive cooling of the trap is required[4]. Nevertheless, according to data obtained by American workers, the best method for the chromatographic determination of micro-quantities of organic substances in air involves the passage of large quantities of the contaminated air (about 10 litres) through active carbon[13] with subsequent desorption of the sorbed trace components by carbon disulphide and analysis of the extract obtained[14]. The efficiency of the adsorption of most organic substances on active carbon is almost 100%, and is not influenced by the volume of the sample nor the rate of sampling. The efficiency of the desorption of organic substances from carbon using carbon disulphide is on the average greater than 90%[15] (according to the data of the National Institute for Occupational Safety and Health (USA)[16] it varies for different substances in the range 81–100%).

The trapping of micro-components from air in a column containing silica gel at ordinary or more particularly at low temperatures is very effective. Silica gel is widely used to concentrate light and heavy hydrocarbons[4], and also organic substances of other classes and inorganic substances[17]. An unsatisfactory feature of silica gel is its highly hydrophilic nature and the incomplete trapping of light hydrocarbons (up to C_3). Thus ethylene is not completely sorbed on silica gel even when the trap is cooled to

−78°C.[4] In this case it is necessary to use more effective sorbents, for example molecular sieves, which are also among the best adsorbents for carbon dioxide[18]. The selectivity of zeolites with respect to various classes of compound and individual substances makes it possible to use them for the directed control and identification of micro-components[10]. A serious disadvantage of these adsorbents is the difficulty of desorbing the trace components, particularly heavy components.

Thermal graphitised carbon black, treated with hydrogen at a high temperature, is also used to concentrate trace components. At low temperatures this non-specific adsorbent makes it possible to trap micro-quantities of organic and inorganic substances, including reactive compounds, from the surrounding air[9].

To extract readily volatile organic substances from air, use is also made of carbon molecular sieves, consisting of highly pure porous carbon, obtained by the thermal decomposition of polyvinylidene chloride[11]. The high adsorption capacity (specific surface approximately 1000 m^2/g), ease of desorption of trace components, and high thermal stability (the adsorbent is stable up to 400°C) make carbon sieves (Carbopacks) valuable materials for filling sampling adsorption tubes. In addition, Carbopacks are extremely hydrophobic.

Other materials which do not absorb moisture include polymeric sorbents, which together with active carbon are most frequently employed to concentrate harmful substances from air in gas-chromatographic analysis[19]. Porous polymeric sorbents are fairly stable to heat, have a high adsorption capacity, and make it possible to sample air at a high rate; the nature of the polymer influences the selectivity of the absorption of micro-components belonging to different classes. Recently, a new highly effective sorbent, "Tenax GC", has been used to concentrate traces of toxic substances from air. This is a polymer of 2,6-diphenyl-*p*-phenylene oxide, which is now often preferred to other adsorbents[20], is less polar than Porapak-S and Chromosorbs, has a very high thermal stability, and is characterised by a non-specific type of adsorption; this is important for the desorption of high-boiling organic compounds. Tenax is used at temperatures up to 400°C; it does not react with most organic substances, and the efficiency of the adsorption and desorption of micro-quantities of organic compounds of different classes is greater than 90%. Another advantage of this polymer, which is used for the analysis of the most varied trace components in air, is the possibility of high-speed sampling (a sample can be taken in 10–20 s)[21] and the high adsorption capacity for compounds of different molecular weight.

Good results in the chromatographic analysis of air have been obtained using sampling devices filled with hydrophobic packing or surface-modified adsorbents or modified (for example by polyethylene) solid carriers[22], which have been used to analyse substances with different boiling points, including polyaromatic hydrocarbons.

One method for concentrating micro-components from air on sorbents involves the removal of a sample on to a moving sorbent (a so-called fluidised bed). This method ensures more uniform distribution of the substances being analysed throughout the volume of the sorbent and also a high rate of sampling (up to 16 litre min^{-1}).[10] The method is a version of the equilibrium concentrating method.

The methods for the absorption of trace components in a concentrating trap, described above, are based on the complete absorption of heavy trace components. A fundamentally new method was proposed by Novak and coworkers[23]. The gas sample was passed through a small concentrator column containing a suitable stationary phase at the temperature of the surrounding medium, until "breakthrough" of the trace components being analysed. Under these conditions, the concentration of heavy trace components in the sorbent along the entire length of the column is in equilibrium with their concentration in the original mixture. In the frontal method of concentration, only part of the layer of sorbent is treated, whereas in the equilibrium concentrating of trace components, the entire volume of sorbent in the trap is used, so that the total quantity of trace components absorbed in the concentrator is greater in this method. From the analytical viewpoint, the equilibrium concentrating method has the following advantages: 1) it is not necessary to measure accurately the volume of gas passed through the trap; it is necessary only to use an excess of gas and to know accurately the temperature of the concentrator; 2) the method makes it possible to increase selectively the sensitivity of the determination of trace components and to avoid the sorption of components which interfere in the determination, by selecting a suitable filler; 3) it is possible to "equalise" the quantities of individual components in the trap, since the distribution coefficients increase in proportion to the increase in molecular weight and the decrease in vapour pressure. The unsatisfactory features of this method include the need to keep the trap and sorbent at a constant temperature, and the possibly incomplete thermal desorption of the specimen.

A method has been proposed[24] for the gas-chromatographic analysis of atmospheric pollutants by saturating a volatile liquid with the air being studied until the equilibrium distribution of the trace components being determined between the two phases (gas–liquid) is achieved, followed by the chromatographic determination of the equilibrium concentration of trace components in the liquid. This method has the following advantages over the equilibrium concentrating of micro-components in non-volatile liquids with subsequent thermal desorption: it does not require a knowledge of the exact quantity of absorbing liquid, it allows repeated analysis from one sample of the concentrator, and it uses volatile solvents of low molecular weight. In some cases it is appropriate to use a non-volatile liquid as solvent.

The chromatographic analysis is sometimes preceded by a concentration based on the condensation (freezing) of trace components. After sampling, the trap is heated, and the trace components are displaced into the chromatographic column by a stream of carrier gas. To increase the efficiency of the condensation of the trace components, it is necessary to increase the cooled surface area of the trap. This can be achieved by increasing the length of the concentrating tube or by filling it with metal or glass spheres or a column sorbent or adsorbent. Since subsequent thermal desorption of the sample is necessary, thermally stable liquids are used as stationary phases for these sorbents[25]. If extensive cooling of the trap is used, micro-quantities of hydrocarbons in air at a level of 10^{-8}% can be determined using a flame ionisation detector[26]. At the temperature of liquid nitrogen, the stationary phase acts not as a solvent but as an absorbent with a low specific surface. The liquid phase is sometimes applied directly to the walls of the concentrator tube, and the impurities concentrated on it are desorbed by heating and collected again in a trap containing molecular sieves, with cooling by liquid nitrogen[27]. This two-stage concentration makes it possible to determine very low concentrations of trace components in air, for example in the study of various biological substrates. The original method provides for direct sampling into the chromatographic

column, the initial section of which is cooled to −78°C.[28] Here, the three stages of the chromatographic analysis of the trace components (sampling, concentration, and introduction of the sample into the chromatographic column) are replaced by a single operation.

A serious disadvantage of concentration methods involving extensive cooling of the concentrator trap is the condensation of water in the traps, leading to a sharp decrease in the adsorption capacity of the sorbent. Thus in the concentration of trace components, a column containing a reagent for the selective absorption of water vapour is placed in front of the trap. The selection of a drying agent is made difficult by the fact that it must retain only water vapour and readily allow the passage of the other components of the mixture being analysed[10]. Heated calcium chloride and magnesium perchlorate are often used to dry specimens of air for analysis[29]. It must be remembered, that Anhydrone irreversibly absorbs nitro-compounds, ethers, nitriles, and unsaturated hydrocarbons. Anhydrous potassium carbonate is a universal and readily accessible drying agent for organic compounds. Hydrocarbons, aldehydes, ketones, alcohols, esters, and many other organic compounds pass practically unchanged through absorbing columns containing potassium carbonate[30].

The temperature of the cooling mixture must be 150–180 K lower than the boiling points of the compounds being trapped from the air. If the temperature is too low, however, aerosols which are not held in the trap may be formed. Thus liquid nitrogen is suitable as a cooling agent only to trap the vapours of compounds which boil at temperatures not exceeding 100°C.[10]

The removal of aerosols and solid particles from air has its own specific features, associated with the fact that they are not absorbed by the usual sorbents. The sampling of aerosols, which represent the form in which most high-boiling hydrocarbons are present in air, and also solid particles (dust, soot) is carried out on fine-fibre filters of glass, plastic, or ceramic[31]. The compounds of the sample collected on the filter are usually extracted in a Soxhlet apparatus, and the resulting solution analysed. Specimens of solid particles carrying various chemical compounds on their surface in the adsorbed state are treated similarly. Aerosols of metals and various inorganic compounds (oxides, salts) are collected on filters of glass fibre or on highly-dispersed fibrous filters of polymeric materials (AFA-V-10 polyvinyl chloride filters).

An important contribution to the theory and development of methods for the analysis of micro-components‡ has been made by the work of Soviet scientists. The methods of chromatography without a carrier gas, many of which were first proposed and developed by Zhukhovitskii and coworkers[32], and which are also called high-concentration gas chromatography, make it possible, under isothermal conditions, to obtain a concentrated zone of both light and heavy trace components at the column outlet. The use of chromatography without a carrier gas, proposed by Zhukhovitskii and Turkel'taub[33], makes it possible to improve and simplify many methods for the analysis of trace components. The method of vacancy chromatography[34] is of considerable importance for the determination of trace components in air and other gases. A high degree of enrichment of the sample in the micro-components being analysed can be achieved by a thermal dynamic method of concentration[35] based on the use of a heater with a negative temperature gradient, moving at intervals along the chromatographic column; the principal component of the mixture being analysed is used as carrier gas. Under the influence of the thermal field, the trace components, which are sorbed more effectively than the principal component, are concentrated, move along the column, and are eluted from it at intervals. The trace component zones become narrower, and sharp separation of the zones takes place. These studies have made it possible to design several forms of chromatograph specially for the analysis of micro-components; these are now produced regularly by Soviet industry, in particular the "Luch" chromatograph, which uses enrichment of the micro-components for analysis on previously evacuated columns[36].

An interesting development of the method of chemical concentration was proposed by Sakharov and coworkers[37], who increased the sensitivity by chemical concentration of the micro-components being analysed, by means of a series of successive chemical reactions.

Since the analysis of micro-components exhibits a whole series of characteristic features, and the determination of trace quantities of harmful substances in air encounters various difficulties, these questions must be examined in more detail. Even in its present form, chromatography represents a method for determining traces (10^{-1}–10^{-7}%) and micro-quantities (below 10^{-7}%) of substances, that is it deals with specimens in the region of 10^{-8} g. At the same time, in some cases it is necessary to detect the compounds being analysed in quantities of 10^{-15} g. In quantitative analysis, the range of concentrations extends from 99.9999% to 10^{-10}%, and in the near future it may be necessary to work at even lower concentrations[5].

The limit of detection of the compounds being analysed is determined by a number of restrictions, namely: 1) non-representative removal of an average sample; 2) the inclusion of new components (contaminants) in the mixture being analysed, at different stages of the analysis (from the sampling device to detection) from foreign sources, and by consequent reactions of the components being analysed; 3) loss of material by selective adsorption during the analysis, and also by chemical reaction; and 4) a decrease in the maximum concentration of a substance during separation.

The problems of the removal of a representative sample are general for all analytical methods and are not examined in the present review. Selective sorption must be examined in more detail. This restriction is associated with the removal of the sample, and a number of factors—temperature, the polarity of the surface and the substances in the sample, their concentration, the degree of turbulence of the flow, and the ratio of the volume to the surface—all influence the results of the analysis. It is particularly difficult to determine traces of non-polar substances present in polar compounds, and also traces of polar substances present in non-polar compounds. The determination of traces of substances at concentrations lower than 3×10^{-6}% depends on the sorptive activity of the surface of the sampling device, which may lead to systematic errors. In this concentration range, therefore, the sampling should be dynamic[5]. In the analysis of micro-components, it is necessary to use special sampling methods, preferably of the continuous type, and special materials for the construction of the containers and connecting tubes; the roughness coefficient of the surface should be close to unity[5,38].

‡ The theory of the analysis and chromatographic separation of micro-components is not discussed in the present work, since it has been examined in detail in a number of papers and in a monograph[10].

Kaiser[5,39] lists the following difficulties in the analysis of trace quantities.

1. The number of individual chemical compounds which may be present in small quantities is extremely large. At concentrations in the region of 10^{-4}%, in addition to the principal component (for example with air) with a concentration of 99%, the maximum possible number of components present in trace quantities is 10000, and in many cases only several hundred can be detected individually. At concentrations in the region of 10^{-7}%, in addition to a principal component at a concentration of 99.9%, the possible number of components present in trace quantities reaches 10^6. All this complicates considerably the analysis and particularly the individual identification of micro-quantities of harmful substances present in air, after their chromatographic separation.

2. The chemical reactivity of a number of components present in trace quantities is extremely high. Many facts indicate that some substances present in concentrations of $\sim 10^{-7}$% cannot be concentrated to 10^{-4}%, since they tend to decompose at these concentrations. This introduces a considerable restriction on the possibility of concentrating micro-quantities of various substances from air.

3. The concentration of stable substances present in a sample in trace quantities may be so low, and the concentration of reactive unstable substances so high, that many attempts to manipulate the sample will systematically lead to a false result.

These difficulties in the analysis of micro-quantities of harmful substances in air cannot always be overcome, but there is now a fairly large number of chromatographic methods which make it possible to analyse atmospheric pollutants with a relative error of not more than 15–20%.

III. DETECTORS. CALIBRATION

Although more than fifty detectors of different types are now used in gas-chromatographic analysis, very few of these have found extensive application for the analysis of atmospheric pollutants. This is due chiefly to the inadequate sensitivity of many detectors, which makes it impossible to carry out the direct determination of ultra-small quantities of substances in air samples. The detailed characteristics and applications of chromatographic detectors for the analysis of micro-components have been described in monographs[40,41] and in a large number of reviews devoted to detectors of different types[42,43] and problems of specific detection[44].

1. Universal Detectors

Of the gas-chromatographic detectors known at present, the flame ionisation detector (FID) is most frequently used in atmospheric and industrial chemistry; the FID is an almost ideal detector for the analysis of micro-quantities of hydrocarbons and most organic compounds. It makes it possible to analyse hydrocarbons at a concentration in air of $\sim 10^{-7}$–10^{-8}%, and when combined with preliminary concentration of the sample, even from small volumes of air, the sensitivity of the determination is increased by an order of magnitude[4]. The FID, which was previously regarded as insensitive to most inorganic compounds[40], also reacts to the presence, in the sample being analysed, of oxygen, nitric oxide, nitrous oxide[45,46], ammonia, phosphine, other oxides of nitrogen and cyanogen[47], oxides of carbon[48], and perfluoroalkanes[49]; it can also be used to determine low concentrations in air of sulphur dioxide, hydrogen sulphide, carbon disulphide, and carbonyl sulphide, mixed with thiols[50]. For example, it is convenient to use the flame ionisation detector, the sensitivity of which for carbon disulphide depends on the rate of flow of hydrogen and the carrier gas, the flame temperature, and other factors, for determining carbon disulphide vapour at concentrations ≤ 0.01%. In this concentration range, the magnitude of the FID signal is directly proportional to the concentration; the formation of ions apparently takes place via the formation, from carbon disulphide, of a small number of $CH^{\cdot}$ radicals, followed by the ionisation reaction $CH^{\cdot} + O = CHO^{+} + e$, characteristic of the operation of the FID.[40,51] By using perfluoromethane (Freon 116) as carrier gas, it is possible to detect sulphur dioxide and carbon dioxide, and also nitrogen and inert gases[52]. The use of ammonia as carrier gas has made it possible to increase considerably the sensitivity of the FID towards chlorinated hydrocarbons[53].

An even more universal detector than the FID is the argon ionisation detector, used for the analysis of many organic and inorganic compounds[40]. The sensitivity of the argon detector towards inorganic compounds of sulphur lies in the range 10^{-6}–10^{-3}%;[54] for phosphine the value is $\sim 10^{-4}$%.[55] The threshold sensitivity of this detector for oxygen, nitrogen, hydrogen, methane, oxides of nitrogen and carbon, and sulphur dioxide is $\sim 10^{-5}$%,[40] although for organic compounds it lies at the sensitivity level of the FID.

Recently, micro-components in air have been analysed using a pyroelectric katharometer, the sensitivity of which is 500 times that of an ordinary thermistor katharometer[50].

2. Selective Detectors

The analysis of atmospheric pollutants is made particularly effective by using selective highly sensitive detectors--electron capture (ECD), thermo-ionic (TID), flame photometric (FPD), and coulometric (COULD) detectors—which make it possible to carry out the qualitative and quantitative analysis of micro-concentrations of pollutants in complex many-component mixtures of substances of different classes. Comparison of the chromatograms obtained using universal detectors (reacting to all components) and selective detectors (reacting to molecules with definite hetero-atoms and functional groups) provides a reliable means of identifying trace components in complex mixtures in atmospheric and industrial air. This method makes it possible, against a background of the hydrocarbons most frequently encountered in polluted air, to determine halogens (ECD), sulphur (FPD), phosphorus (TID), etc. Combinations of FID and ECD, FID and FPD, and FID and COULD are particularly effective. The mass-spectral detector[40] has a unique selectivity.

The most sensitive detector in gas chromatography (see Table) is the electron capture detector[57], which, in spite of its short linear range, is widely used to determine halogens, sulphur-, nitrogen-, and halogen-containing organic compounds, and also metal aerosols (as chelate or organometallic compounds) in air[58,59]. This is one of the few detectors which can be used to determine nitrogen dioxide[60], inorganic compounds of sulphur[61], and other reactive substances by the direct method at concentrations of $\sim 10^{-7}$–10^{-4}%.[62] The ECD can be used to detect micro-quantities of polyaromatic hydrocarbons[63]; in the determination of meteorological tracers, for example sulphur hexafluoride, in the atmosphere, the sensitivity of the analysis reaches the phenomenal value of 2×10^{-10}%.[64]

The very high sensitivity of the ECD towards compounds of the halogens (which increases with increased number of halogen atoms in the molecule), and in particular to pesticides[65], has made this detector irreplaceable in the analysis of residual quantities of pesticides in the environment.

Sensitivity and selectivity of the detectors most frequently used for the analysis of pollutants in air.

Detector	Selectivity*							Threshold sensitivity, wt.%	Refs.
	N	S	Hal	O	P	hydrocarbons	OMC		
FID	–	–	–	–	–	–	–	10^{-8}	40, 41
Mass spectrometer	–	–	–	–	–	–	–	10^{-8}	40
ECD	+	+	+	+	+	PAH	+	10^{-9}	58, 63
TID	+	–	+	–	+	–	–	$5\cdot10^{-9}$	63, 74
FPD	–	+	+	–	+	–	+	10^{-8}	71, 72
COULD	+	+	+	–	+	–	–	10^{-7}	76
Detector with microwave radiation	–	+	+	–	+	+	+	10^{-8}	63, 80
Spectrofluorimetric detector	–	–	–	–	–	AH PAH	–	10^{-5}	40, 63

*Symbols: PAH = polyaromatic hydrocarbons; AH = aromatic hydrocarbons; OMC = organometallic compounds. The "plus" symbol indicates the class of compound to which the given detector is most sensitive.

The FPD is also frequently used for this purpose. The FPD has a high selectivity and is used for the analysis of such atmospheric pollutants as sulphur-, phosphorus-, nitrogen-, and halogen-derivatives of hydrocarbons, oxides of nitrogen and sulphur, hydrogen fluoride, nitrogen fluorides, carbon disulphide, and metals (as chelate compounds)[40,63,66]. The FPD has been used to determine nanogram quantities of the halogens and alkyl halides[67,68] and 10^{-1}–10^{-8}% of volatile compounds of sulphur and phosphorus[60,70], and a combination of an FPD and an FID makes it possible to analyse separately, in atmospheric air, micro-quantities of sulphur-, chlorine-, phosphorus-, and nitrogen-containing compounds[71]. The chief characteristic of the FPD and its use for the analysis of volatile compounds of sulphur in air have been described[72]. This detector makes it possible to determine, in polluted air, ~ 10^{-7}% of sulphur dioxide, hydrogen sulphide, carbon disulphide, carbon oxide sulphide, sulphides, and thiols[73].

Ultra-small quantities of substances containing phosphorus, nitrogen, and halogens can be detected using the TID, the threshold sensitivity of which is 2×10^{-6}% for chlorine, 10^{-8}% for nitrogen, and 5×10^{-9}% for phosphorus[40,74]. Thus the TID, together with the ECD, is used for the analysis of residual quantities of pesticides, and also to determine toxic organic compounds of nitrogen and chlorine in air[41,75].

The COULD has a high sensitivity towards compounds of sulphur, nitrogen, the halogens, and phosphorus[63]. It has been used to determine micro-quantities of the halogens, sulphur dioxide, and hydrogen sulphide (10^{-5}%) in air[76]. The COULD, like other selective detectors (ECD, FPD, TID), has an extremely low sensitivity towards hydrocarbons (lower by 3–5 orders of magnitude than that for heteroatoms).

Among the other detectors used to determine traces of harmful substances in air, the helium ionisation detector has a high sensitivity. It makes it possible to analyse the permanent gases, various light compounds of sulphur, and light hydrocarbons (~ 10^{-7}%)[77], and also to determine low concentrations of chlorine and Freons in air[78].

In the analysis of air, increasing use is being made of sensitive spectral detectors, the selectivity of which may vary over a wide range; for example, the emission spectrometer[79], a detector using microwave radiation[80], and a spectrofluorimetric detector, selective towards aromatic compounds[63]. A very valuable detector for the gas-chromatographic analysis of micro-components is the mass spectrometer, the sensitivity of which is comparable to that of the FID.[40] A combination of gas chromatography and mass spectrometry makes it possible to determine very low concentrations of toxic substances in air, and this method is now preferred to all other methods for identifying traces of a substance leaving a chromatographic column[81].

3. Preparation of Standard Mixtures and Calibration

The magnitude of the signal of differential detectors depends to a considerable extent on the nature of the compounds being analysed. Thus to carry out accurate quantitative determinations it is necessary to know the individual sensitivity of the detecting assembly with respect to the substances being analysed. For the calibration, that is for the determination of the quantitative relationship between the instrument signal and the absolute concentration of a component, it is necessary to have mixtures of the compounds being analysed with known concentrations, that is standard mixtures. The basic principles, methods, and characteristic features of the calibration of chromatographic detectors has been examined in detail[40,41,43] and are well known.

Static methods for preparing these mixtures are simple and most convenient for gaseous and volatile substances. The simplest involves the use of gas-measuring devices of known volume, glass bottles, and other containers, into which an accurately known quantity of the substance or mixture of substances being analysed is introduced[82,83]. Static methods of calibration are characterised by a large number of possible sources of error, and are therefore less reliable than dynamic methods; the chief disadvantage of static methods of preparing standard mixtures is the adsorption of micro-components on the walls of the containers (in some cases the losses may reach 50%[10]).

The dynamic method of calibration, which does not have these disadvantages, is used much more frequently in analysis. The simplest version of this method involves the dilution (sometimes in several stages) of pure cylinder gases, which are not always available, however. Here it is necessary to have a special measuring apparatus which makes it possible to control the gas flow rate very accurately[84]. The National Bureau of Standards (USA) has developed an apparatus for creating micro-concentrations of hydrogen fluoride, arsine, and phosgene by dilution[85]. The method makes it possible to obtain mixtures with a concentration of substances in the range 0.5–5 times the MPC. The method of exponential dilution[86], previously proposed by Lovelock[10], makes it possible to decrease considerably adsorption on the walls of the container and to prepare very low concentrations of several substances simultaneously. For the production of ultra-low concentrations in a stream or in a closed volume, a method based on the electrochemical preparation of the components of

the mixture being produced[87] is of interest. A significant advantage of this method is the absence of parts subject to friction and the ease of control of the rate of liberation of the gas being calibrated, by changing the current strength through the electrolyte.

The method of preparing standard mixtures of micro-quantities of different substances, based on the diffusion of the gases or vapours of liquids into the stream of diluent gas (carrier gas), is most widely used. The diffusion may take place through a tube, a porous surface (glass or ceramic), or a polymer film; in diffusion methods, sorption on the walls of the vessels is not significant. The use of diffusion cells makes it possible to calculate the concentration of the mixture, but the accuracy of the dosage and the reproducibility of the method are not always satisfactory[88].

The ability of micro-components to diffuse through the walls of plastic tubing has aroused considerable interest among analytical chemists[89]. It has been found that the stationary rate of diffusion of gases through the walls of tubes of ethylene and propylene Fluoroplasts at a constant temperature is practically constant, depending to slight extent on the composition and pressure of the gas. The rate of diffusion (and hence the concentration of micro-components obtained) is determined from the decrease in the weight of the tube containing the liquefied gas. The method of preparing standard mixtures of micro-concentrations of different substances based on this phenomenon has been widely used. The permeability of polymer tubes to different substances has been studied[89,90]. Diffusion through Teflon has been used to prepare standard mixtures of hydrogen sulphide, carbon disulphide, hydrogen fluoride, chlorine, ammonia, phosgene, propane, and methanethiol in air[91,92]. The method of preparing the filling the diffusion tubes has been described[93]. Diffusion through a Teflon tube may be constant for several years, and the total error of this dosage method does not exceed 1–2%.[94] The preparation of mixtures of moist air containing oxides of carbon, sulphur, nitrogen, ammonia, chlorine, hydrogen chloride, and other gases has been described[95]. The construction of an apparatus for the accurately controlled dilution of a gas specimen using semi-permeable polymer membranes has been discussed[96]. For this purpose, use has also been made of silicone rubber, which passes the vapours of organic substances at a rate directly proportional to the surface area of the tube and inversely proportional to its wall thickness[97].

A simple method for preparing micro-concentrations of chlorine and nitrogen dioxide involves the saturation, by these gases, of BAU active carbon, from which the gases can be desorbed to give concentrations of the gases at the level of the MPC, which remain constant for a prolonged period[98]. Various experimental problems in the preparation of standard mixtures and the calibration of chromatographs have been discussed in various papers[99,100] and a monograph[13]. An interesting review of methods for preparing standard mixtures at ultramicro-concentrations has been published[101]. The theory of the principal methods for calibrating instruments for gas analysis (in particular chromatographs) has been described in detail[102].

IV. CHARACTERISTIC FEATURES OF THE QUALITATIVE AND QUANTITATIVE ANALYSIS OF MICRO-QUANTITIES OF HARMFUL SUBSTANCES IN AIR

The principal methods for identifying micro-concentrations of harmful substances in complex mixtures in polluted air, used in conjunction with gas chromatography, have been examined in detail[63]. The most promising method for the qualitative analysis of micro-components in complex mixtures of organic and inorganic compounds of different classes is undoubtedly the combination of gas-chromatographic separation with mass-spectral analysis of the individual components of the sample, leaving the chromatographic column (GC-MS). This method of identification gives the most reliable results and is widely used in the analysis of atmospheric air and the air in living quarters and in industrial plants (gas liberation from polymers, rubber, plastics, etc.). After sampling and preliminary treatment, the sample is introduced into the gas chromatograph–mass spectrometer system[103], and the results of the analysis are processed on a computer[104]. The method is expensive and complex, but is being used on an increasing scale for the control of pollutants in the environment, particularly in those cases where the polluted air contains many-component mixtures of toxic substances.

Simpler methods are now being used for the same purposes, and these methods, taken together, may give more or less identical information on the composition of complex mixtures of chemical substances. One such method is the chromatographic-distribution method of identifying volatile organic compounds[105]. This method makes it possible to carry out the qualitative and quantitative analysis of organic substances (dissolved in an absorbing liquid) from the relative distribution coefficients in a liquid–liquid system (K_{rel}). The value of K_{rel} is determined by gas chromatography from the results of the analysis of aliquot portions of both liquid phases.

Various methods for the qualitative analysis of micro-components after chromatographic separation of the compounds in the sample have been described[63,106]. For this purpose it is also possible to use purely chromatographic methods, identifying the substances in the sample from their retention characteristics[107–109] and from their logarithmic relationships[63,110] or by reaction gas chromatography[63,111–113] and various other methods of analysis[114].

Sometimes, the components leaving a chromatographic column are identified using colour reactions for individual functional groups in organic compounds[63], but their sensitivity (0.1–1.0 μg)[115] is often insufficient (in analysis on capillary columns and in various other cases when small samples are being analysed). The infrared spectrum of a substance provides a reliable method for its identification. The successful use of this method to characterise individual substances after chromatographic separation is difficult, however, in the case of micro-components, and is fairly infrequently encountered in the analysis of air, due to the difficulty of accumulating a sufficient quantity of substance (20–30 mg) to obtain infrared spectra[63]. A spectrometer can also be used directly as a gas-chromatographic detector, but this requires a special analytical technique (spectrometer connected to the chromatograph, special cells, etc.)[116].

The successful identification of micro-quantities of harmful substances in complex mixtures in polluted air depends largely on the completeness of the separation of the compounds being analysed in the sample. Thus the chromatographic separation of toxic substances in air samples is carried out using capillary packed columns containing selective liquid phases[117] or highly efficient capillary columns[118]. The characteristic features of the identification and quantitative analysis of micro-components in air have been examined[10,119,120].

It has been shown[121] that the analysis of various aromatic hydrocarbons at a concentration of 10^{-7}% from one litre of air can be carried out with an accuracy of ±25%.

The accuracy of the analysis depends on the complexity of the system used for sampling, concentrating, preparation of the sample for chromatographic separation, and the chosen method of calibration. The use of even a moderately complex concentrating system may in itself introduce an additional source of errors in all analytical operations[4]. To increase the accuracy of the chromatographic analysis of atmospheric pollutants, it is necessary to use special vapour–gas mixtures as standards, and also to measure the rate of flow of air by means of additional flow-meters in the dosage systems[99,101]. The methods of calculation used in chromatography and the question of the accuracy of chromatographic analysis have been discussed[122,123].

V. ANALYSIS OF INORGANIC SUBSTANCES

The principal inorganic atmospheric pollutants are the oxides of carbon, nitrogen, and sulphur, hydrogen sulphide, and the halogens, the main sources of which are industrial emission and automobile exhaust. In addition, atmospheric dust contains highly toxic oxides and aerosols of metals (lead, mercury, beryllium, etc.). The compositions of inorganic industrial poisons are determined by the specific features of the production process (inorganic synthesis, metallurgy, textile production, etc.). Various problems of the chromatographic analysis of micro-quantities of harmful inorganic substances in air have been discussed[4,124].

1. Halogens and Their Compounds

The determination in air of micro-concentrations of the halogens and their derivatives, which exhibit an appreciable toxicity, involves familiar difficulties, associated chiefly with the high reactivity of these substances: they react with the material of the traps, the chromatographic packing, the connecting tubes of the chromatographs, and the detectors used. This can be partly avoided by using apparatus constructed from corrosion-resistant materials and by using inert sorbents and stationary phases stable towards reactive compounds. Nevertheless, an unavoidable feature of the analysis of traces of corrosive and reactive substances is the prolonged conditioning of the chromatographic apparatus and sorbents in contact with the gases being analysed[9]. All these problems in the chromatographic analysis of air have been discussed in detail[9,124–127].

The gas-chromatographic determination in air of the extremely reactive fluorine and most of its compounds is carried out using completely inert sorbents and liquid phases (chlorofluorohydrocarbons and polymers based on them), and the parts of the chromatographic apparatus (columns, connecting tubes, detectors) are made of Teflon and pure nickel and its alloys[124]. The methods of sampling air contaminated by fluorine-containing inorganic compounds have been examined[128], but there is very little published information on the gas-chromatographic determination of fluorine in air, and this generally relates to the analysis of not fluorine, but its derivatives, for example triethylfluorosilane[129]. The very reactive chlorine trifluoride, which is liberated from liquid oxidants in the transport of rocket fuel, has been determined (at a concentration of 5×10^{-6}%) on a chromatograph with an ECD on a packing containing a methylsilicone oil after separation from air and halogens[130]. Analyses of this kind cannot be carried out on columns with halogen-containing stationary liquid phases, since the ECD is very sensitive to halogens.

The analysis of chlorine and hydrogen chloride does not require such rigorous conditions. These substances are separated on ordinary stationary phases[124], but particular care is necessary with the very unstable chlorine dioxide, particularly during its concentration[9]. The quantitative determination of the MPC of chlorine and nitrogen dioxide in the presence of other reactive gases has been described[131].

The conditions for the gas-chromatographic determination of various reactive gases in air have been examined in detail[132]. It was established that by using an ECD it is possible to analyse 10^{-4}–10^{-5}% of chlorine and oxides of sulphur and nitrogen with a relative error of ~ 10%, although for nitrogen dioxide the error may reach 50%.

The chromatographic analysis of phosgene presents no particular difficulty, and the use of an ECD makes it possible to analyse this gas in mixtures with chlorinated hydrocarbons in concentrations of ~ 10^{-6}–10^{-7}%[133]. The high sensitivity of the ECD makes it possible to analyse air for ultramicroconcentrations of sulphur hexafluoride and various other tracers used to study the propagation of air currents in the atmosphere and various pollutants in the troposphere (lower atmosphere)[64].

2. Compounds of Nitrogen

Among many methods for the analysis of oxides of nitrogen[134,135], their gas-chromatographic determination in air has recently been widely used[136], but at present this method is not preferred, because the chromatographic analysis of micro-quantities of oxides of nitrogen, particularly nitrogen dioxide, encounters a whole series of difficulties, associated with the high reactivity of these compounds. For the analysis of micro-concentrations of nitrogen dioxide, it is best to use glass columns and inert stationary phases based on chlorofluorohydrocarbons[137]. However, prolonged conditioning of the chromatographic packing in the presence of oxides of nitrogen makes it possible to analyse these and other reactive gases on ordinary stationary phases, for example diethyl phthalate[131]. Various chromatographic columns and detectors used for this purpose have been discussed[138]. The detection of nitrogen dioxide by a katharometer after preliminary concentration of the sample makes it possible to determine ~ 10^{-4}% of this gas in air[131]. A similar result is obtained in the direct determination of oxides of nitrogen using an ECD[139].

In view of the difficulties of the direct analysis of micro-quantities of nitrogen dioxide, the methods of reaction gas chromatography have been increasingly used in recent years for this purpose. By using an ECD, it is possible to determine with a high sensitivity the products of the reaction of oxides of nitrogen with phosphines or phosphites[140], styrene, or xylenes[141]. The conversion of nitrogen dioxide into nitrobenzene and the determination of the latter (10^{-12} g) using an ECD has been described[142].

The analysis of oxides of nitrogen in the atmosphere is further complicated by the fact that, under the influence of sunlight, they react with hydrocarbons, forming in the smog an even more reactive mixture of ozone, peroxyacetyl nitrate, and peroxybenzoyl nitrate. Methods for sampling air and for the chromatographic analysis of

oxides of nitrogen in the atmosphere in the presence of oxides of sulphur and carbon, oxidants, and hydrocarbons have been described[143,144].

Equal difficulties are encountered in the chromatographic analysis of nitric oxide, which is usually present in air mixed with other oxides of nitrogen[140]. The accuracy of the analysis can be improved by the quantitative removal of nitrogen dioxide in a special column using 2,2',2''-nitrilotri(ethanol) on a diatomite carrier[145]; to increase the sensitivity, the products of the reaction of nitric oxide with sodium butoxide are detected using an FID.[146]

The determination of nitrous oxide in atmospheric air presents no difficulties, and is generally carried out by gas-adsorption chromatography[147]. An interesting feature is that with increase in temperature from 20°C to 400°C the sensitivity of the ECD towards nitrous oxide increases by a factor of 1000. This phenomenon can be used to monitor low concentrations of nitrous oxide in the atmosphere[147].

The electron-capture detector makes it possible to determine 10^{-7}% of nitrates and nitrites in air and in biological media after conversion to nitrobenzene[148]. The direct chromatographic analysis of ammonia, particularly in the presence of moisture, is complicated by the spreading of the peak corresponding to this substance on most available packings[149]. The determination of ammonia in cigarette smoke has been described[150]; ammonia has been detected together with other gases in the products of the combustion of plastics[151].

Similar mixtures of inorganic gases, also containing cyanide vapours, are encountered in industrial air contaminated by the products of the combustion of polyurethanes[152]. Micro-quantities of hydrogen cyanide and cyanogen (~ 10^{-4}%) have been determined in air using an FID after the separation of hydrogen cyanide from other gases on a column containing Carbopacks on Teflon[153]. A method has been described for removing cyanide vapours on silica gel with subsequent extraction of the sample by methanol and chromatographic analysis of the resulting solution at room temperature on a column containing adiponitrile on celite[154]. Traces of cyanogen chloride in air have been determined using an ECD[155].

3. Compounds of Sulphur and Phosphorus

Inorganic compounds of sulphur are sampled and concentrated using cooled traps containing column packings[156] or concentration columns containing 13X molecular sieves[157] or active carbon[158] as adsorbents. In the last case, the sample is extracted from the column using benzene, and analysed on a chromatograph with a flame photometric detector.

In the analysis of compounds of sulphur, glass or Teflon columns are used[159], and Porapak-S is successfully used as sorbent for the chromatographic separation. Columns containing different packings, previously conditioned by the gases being analysed, are also used. The best solid carriers are Chromosorb W and porous polymeric sorbents, on which various liquid phases (chiefly polar phases) are deposited[160]. In the opinion of some authors[161], the separation of organic compounds of sulphur, hydrogen sulphide, sulphur dioxide, and carbonyl sulphide present in air in very low concentrations is best carried out using chromatographic columns containing Carbopacks, treated with a solution of phosphoric acid and nitrylsilicone XE-60.

Gas-chromatographic methods for determining micro-quantities of carbon disulphide and carbon oxide sulphide[158] and hydrogen sulphide[162], and the analysis of complex mixtures of inorganic compounds of sulphur in the atmosphere[163], in the neighbourhood of a cellulose and paper plant[164], in the effluent gases from plants producing starch[165], and in sulphuric acid manufacture[166] have been described.

Cryogenic gas chromatography has recently been used for the analysis of atmospheric pollutants. Traces of the oxides of nitrogen, carbon, and sulphur, hydrogen sulphide, carbonyl sulphide, and light hydrocarbons are much more effectively separated on ordinary chromatographic packing at low temperatures[167].

Elemental phosphorus in air is determined by trapping it in an absorber containing xylene and analysing an aliquot portion of the solution on a chromatograph with an FPD[168]. Phosphine can be determined in air at a concentration of 10^{-7}% using ionisation detectors[169].

4. Permanent Gases

The permanent gases and other low-boiling gases are generally analysed by gas-adsorption chromatography, since the solubility of these gases in the liquids used as stationary phases in gas-liquid chromatography is usually too low. Most work on the chromatography of the permanent gases has been devoted to the determination of the oxides of carbon, liberated into the atmosphere in various processes of fuel combustion and in forest fires.

The chromatographic separation of micro-quantities of the permanent gases is usually carried out using active carbon, molecular sieves, and porous polymers as adsorbents[124]. For the analysis of mixtures of substances having a wide range of boiling points (permanent and inert gases and hydrocarbons), 2–3 columns with different adsorbents are used[170].

In recent years, several detectors have been described, which make it possible to determine with a high sensitivity (10^{-4}–10^{-5}%) the oxides of carbon and other permanent gases in the atmosphere and in industrial air. These include discharge detectors[171], ultrasonic detectors[172], and the pyroelectric katharometer[173]. The last detector can be used to detect reliably 5×10^{-5} vol.% of carbon monoxide with a relative error of not more than 5%. A high sensitivity in the determination of CO can also be achieved using a detector of low sensitivity. In this case the carbon monoxide present in a sample of several litres of air is concentrated by extensive cooling on a column containing CaA zeolite[174]. By concentrating the CO in stages, it is possible to determine less than 10^{-6}% of carbon monoxide[175]. Nevertheless, the analysis of micro-concentrations of carbon monoxide (and sometimes also carbon dioxide) is most frequently carried out by catalytic hydrogenation of CO to methane with subsequent detection of the CH_4 on an FID.[176] The sensitivity of this method is ~ 10^{-5}%; an unsatisfactory feature is the low accuracy and the time taken for the conversion.

The chromatographic determination of micro-quantities of carbon dioxide is carried out using columns containing silica gel and other adsorbents[177]. In addition to the analysis of atmospheric air[178], gas chromatography is used to determine CO,[179] CO and CH_4,[180] and CO and light hydrocarbons[181] in respirator gases, and also to analyse air in sealed isolated compartments[182] and mines[183].

Gas chromatography can also be used to determine traces of ozone, separated from air and chlorine on silica gel at low temperatures, and detected using an ECD ($\sim 5 \times 10^{-3}\%$) [184] §.

5. Metal Aerosols

The ability of various metals to form volatile complex compounds with organic ligands, particularly chelate compounds [185], has made it possible to use gas chromatography to determine the aerosols of various toxic metals and their compounds in air.

Only a few minutes are required for the chromatographic analysis of picogram quantities of aluminium and chromium as their chelate compounds with trifluoroacetylacetone (TFA) [186]. The methods of sampling and the conditions for the separation and chromatographic analysis of highly toxic aerosols of metallic beryllium and its compounds have been described [187]. The air being analysed was passed through a filter, the aerosols retained were ashed with the filter and dissolved, and a solution of TFA in benzene was added. An aliquot portion of the benzene solution of the resulting $Be(TFA)_2$ was analysed on a chromatograph using an ECD, which makes it possible to determine metal chelate compounds with a very high sensitivity (10^{-10} g aluminium, 10^{-12} g chromium, and 10^{-13} g beryllium) [188].

VI. ANALYSIS OF ORGANIC SUBSTANCES

1. Readily Volatile Hydrocarbons

Methods for the gas-chromatographic analysis of micro-quantities of hydrocarbons in air have been fairly well developed and described in detail [4,189,190]. The substances present in a sample of polluted air are usually concentrated on a suitable adsorbent (silica gel, active carbon, polymeric sorbents) at the temperature of the surrounding medium (or with cooling), or trapped in a concentrator containing an inert packing at low temperatures, and the separation and analysis are carried out using various sorbents and a flame ionisation detector. For the overall determination of hydrocarbons and other organic substances in air [191], the sample being analysed is introduced directly into the FID. For the separate determination of the light hydrocarbons (C_1–C_4), gas-adsorption chromatography is used, with active carbon, silica gel [192], molecular sieves [193], or Porapak-S [194] as adsorbents. Micro-quantities of heavier hydrocarbons (beginning from $\sim C_5$–C_6) are analysed by gas-liquid chromatography, and several dozen liquids of different polarity are used as stationary phases.

Gas chromatography can be successfully used to analyse samples of polluted air of complex composition containing, in addition to hydrocarbons, their derivatives containing atoms of oxygen, nitrogen, sulphur, and halogens. Mixtures of industrial poisons of this kind are liberated into the air of industrial plants in the preparation, processing, and storage of polymers and technical compositions based on them, and also in the pyrolysis of these materials under different conditions [195,196]. A combination of chromatographic columns with stationary phases of different polarity has made it possible to separate and identify the components of the gases liberated in the vulcanisation of rubber [197] and in rubber mixing [198], and the combination of gas chromatography and mass spectrometry has given detailed information on the composition of the volatile products polluting air when various rubbers are heated [199].

The possibilities provided by gas chromatography in the study of toxic products in atmospheric and industrial air have been extended considerably by the use of highly efficient capillary columns. Approximately 100 paraffinic, naphthenic, and aromatic hydrocarbons have been determined in the air of industrial plants containing white-spirit vapour. The analysis was carried out on a chromatograph with a 70-metre capillary column containing squalane at 100°C [200-202]. A mixture of alkylbenzenes liberated into the air by plants producing polystyrene has been studied similarly [203]. Complex mixtures of hydrocarbons and their derivatives, polluting the air in the production of rubber footwear, have been separated on capillary columns and identified by various physicochemical methods [204]. The use of temperature programming on capillary columns containing silicones has made it possible to separate and identify up to 200 C_3–C_{12} hydrocarbons present in the gases emitted from automobile and diesel engines [205]. The absolute quantity of soot in treated automobile gases has also been determined by gas chromatography after trapping the soot by means of a sitall (glass ceramic) filter and pyrolysis of the sample [206], and the highly toxic tetra-ethyl-lead has been determined in air at a concentration of 1 mg m^{-3} using an ECD [207].

Particularly valuable information on the composition of atmospheric pollutants is given by the combination of gas chromatography and mass spectrometry. This method has been used to determine the concentration of organic pollutants in industrial and city air [208,209]. The sample of air being analysed was passed through a drying agent and a cooled trap containing Tenax GC [210] or Chromosorb W, impregnated with a silicone [211]; the concentrated components were displaced from the trap by heating, into a capillary column connected to the mass spectrometer.

2. Vapours and Aerosols of Hydrocarbons with a Low Volatility

The chromatographic analysis of hydrocarbons with a high molecular weight encounters certain difficulties associated with the sampling, separation, and detection of high-boiling compounds. Organic pollutants of high molecular weight in the form of aerosols, and also adsorbed on dust particles suspended in air, are trapped by mechanical or electrostatic filters and fractionated by extraction or thin-layer chromatography. Methods for isolating organic substances from aerosols and dust, and apparatus and procedures for the analysis of atmospheric pollutants of this kind have been described [212,213].

More than 100 organic substances (C_6–C_{20}) have been identified in city air after passing the sample through a cigarette filter of active carbon or through a column containing graphitised carbon black, with subsequent extraction of the sorbed compounds by carbon disulphide and chromatographic analysis of the substances liberated on a capillary column with a silicone liquid phase [214]. The components of these complex mixtures are identified by the usual chromatographic–mass-spectrometric method [214,215].

Gas chromatography has been used increasingly in recent years to solve the important problem of determining the concentration in air of polycyclic aromatic hydrocarbons (PAH), many of which are carcinogenic. The PAH

§ See also Ref. 340.

present in air, which are usually adsorbed on dust particles, are concentrated on active carbon[216] or collected on a glass fibre filter[217]; they are then extracted by benzene, cyclohexane, or nitromethane, and subsequently analysed by gas chromatography. A simple apparatus for the effective collection of samples of this kind, consisting of a condenser coil containing Tenax GC, has been described[218]. Micro-concentrations of PAH are now successfully separated using modified sorbents. A short column containing celite-545, the surface of which is covered by linear polyethylene, with temperature programming from 70°C to 290°C, can be used to separate 16 polyaromatic hydrocarbons[219], and even to separate such pairs as phenanthrene and anthracene, chrysene and benzanthracene, and perylene and 3,4-benzpyrene. Equally effective results were obtained using a column containing graphitised carbon black[220], and also carbon black impregnated with a small quantity of a polyphenyl ester[221]. This packing makes it possible to separate 3,4- and 1,2-benzpyrenes in 30 min, and anthracene and phenanthrene in 2–3 min (at 320°C).

The combination of gas-chromatographic separation with spectrofluorimetric detection has a high selectivity in the analysis of PAH[222]. The fluorimetric detector, the sensitivity of which with respect to fluorene is not less than 5 ng, can be used to detect selectively even PAH peaks which overlap on the chromatograms[223]. An even greater increase in the selectivity of this analysis can be achieved by preliminary separation of the PAH from the air sample by thin-layer chromatography[224]. Approximately 40 new PAH have been identified in air after separating an extract of the sample by liquid chromatography on a column containing silica gel, with subsequent gas-chromatographic analysis on a capillary column using a mass spectrometer[225]. This method has been used particularly frequently in recent years, and the polyaromatic compounds have been identified by a combination of gas chromatography, mass spectrometry, nuclear magnetic resonance, and computer calculations[226].

Progress in the gas-chromatographic analysis of polynuclear hydrocarbons in recent years has been discussed[227], and it has been pointed out that the extraction of the PAH sample from glass fibre filters, carried out in a Soxhlet apparatus, takes a long time and has a low reproducibility, and liquid-phase extraction using ultrasonics, or the even more effective gas-phase extraction, have been recommended for this purpose.

3. Oxygen-containing Organic Compounds

One of the most toxic atmospheric pollutants is peroxyacetyl nitrate (PAN), which is formed together with other compounds in the photolysis of automobile exhaust gases or as a result of atmospheric photochemical reactions involving hydrocarbons and oxides of nitrogen. Reactive PAN and alkyl nitrates are analysed using a glass or Teflon column with a packing of polyethylene glycol on Chromosorb W, and an ECD, which selectively detects PAN in mixtures with hydrocarbons[228,229]. The same methods are used to analyse toxic nitroalkenes[230], peroxypropionyl nitrate, and peroxybenzoyl nitrate[231].

Micro-quantities of polar aldehydes, ketones, and alcohols have been separated from hydrocarbons using a sectional chromatographic column containing OP-7 detergent and the highly polar cyanoethoxypropane, which are also present in the packing of the enriching column[232]. The determination of aldehydes and ketones in air by gas chromatography has been described[233,234]. In the analysis of alcohols and esters, a liquid absorber containing an alcohol or n-paraffinic hydrocarbons, or a column containing active carbon or silica gel, are used as concentrators[235]. The use of water for the selective extraction of C_1–C_4 alcohols adsorbed on carbon makes it possible to separate them from other compounds in the sample[236]. Chromatographic methods have been developed for the analysis of phenols in air; the phenols are separated on capillary and packed columns[237,238]. For the separate determination and identification of carboxylic acids, the air is passed through a glass fibre filter impregnated with alkali, or through a column containing silica gel; alternatively, the acids are absorbed by a solution of sodium hydroxide[239]. Capillary columns containing squalane and XE-60 cyanosilicone have been used to determine the composition of a complex mixture of oxygen-containing volatile substances (aldehydes, alcohols, carboxylic acids), contaminating air as a result of the decomposition of resin[240].

4. Organic Compounds of Sulphur and Phosphorus. Pesticides

Gas-chromatographic methods for determining volatile organic and inorganic compounds of sulphur using different detectors and different packing have been reviewed[241]. The sulphur compounds are trapped from the air in concentration tubes containing silica gel, active carbon, or Tenax GC[242,243]. Micro-quantities of organic compounds of sulphur are generally separated using the same packing as in the analysis of hydrocarbons, and the preferred detector is the FPD, which has a high sensitivity and selectivity to volatile compounds of sulphur[244]. Gas chromatography has been used to analyse sulphur-containing odourants and to determine other pollutants with a strong odour in air[245], and also for the analysis of traces of the highly toxic dimethyl sulphate[246].

The chromatographic analysis of organic compounds of phosphorus has been reviewed[247]. Gas chromatography is now the most sensitive and most convenient method for analysing the environment for pesticides, most of which are organic compounds of phosphorus and chlorine[248]. Most organic pesticides are fairly volatile, so that they can be separated in the vapour phase at temperatures up to 250°C. The methods of air sampling and the quantitative chromatographic analysis of pesticides have been discussed[249,250]. Micro-quantities of pesticides are analysed on glass columns (to avoid the decomposition of complex halogen-containing molecules) containing different packing, usually with silicone stationary phases[251,252]; glass capillary columns combined with an ECD are also used[253]. After enrichment of the sample, the sensitivity of the determination of pesticides using an ECD may reach 1 ng m^{-3} air[251]. The TID is extremely selective and sensitive to phosphorus-containing pesticides, and is now being used successfully to determine these substances in air[254].

5. Halogen-containing Organic Compounds

Fluorinated hydrocarbons[255], chlorofluorohydrocarbons[256], and fluoro-organic acids[257] in air are determined by gas chromatography using an ECD. In addition, a large number of recently published papers describe the chromatographic analysis of chlorinated hydrocarbons, particularly the determination of the highly toxic vinyl

chloride. Methods for determining chlorinated hydrocarbons, proposed as standard methods, have been described[258]. Organic chlorine-containing compounds are most frequently concentrated in short columns containing active carbon[259], from which they are desorbed by heating or extracted by an organic solvent; silicones, hydrocarbons, and phthalates are generally used as stationary phases for the separation of these compounds.

Micro-quantities of halogenated hydrocarbons are usually detected using the COULD and ECD[260,261], and the latter is an almost ideal detector for the analysis of halogen-containing substances. It is practically insensitive to hydrocarbons, whereas its sensitivity towards various organic compounds of chlorine may reach 8.5×10^{-11}%.[262] At the same time, the FID is most frequently used for the analysis of vinyl chloride (one chlorine atom in the molecule)[263]. Samples of air contaminated by vinyl chloride are obtained using Tenax GC or other adsorbents, the best of which is active carbon. If carbon disulphide is used as extracting agent, the efficiency of the desorption of vinyl chloride from carbon is greater than 90%.[264]

Gas chromatography has been used to analyse chlorine-containing pesticides[265], complex mixtures of Freons[266], polychlorobiphenyls[267], and other chlorine-containing organic pollutants of atmospheric and industrial air[268].

6. Nitrogen-containing Organic Substances

1 mg m^{-3} of the isomers of nitrotoluene can be determined by passing 20 litres of air through an absorber containing ethanol[269]. The gas-chromatographic analysis of air contaminated by benzene, chlorobenzene, nitrobenzene[270], and volatile N-nitroso-compounds has been described[271]. Nitriles, to which the ECD and FID are equally sensitive, are determined using the second of these detectors, by means of which it has been possible to detect 5×10^{-5}% of acrylonitrile in 1 ml of sample[272,273]. Micro-concentrations of 2,4-toluenedi-isocyanate have been determined in air using an ECD[274]. The accuracy of the chromatographic determination of mono-, di-, and trimethylamines in air using the FID is not less than 15%, and the sensitivity of the analysis is ~ 0.2 mg m^{-3}.[275,276] Good results are obtained by concentrating and separating amines on columns containing Tenax GC[277]. The flame ionisation detector has also been used to determine micro-quantities of aniline[278], pyridine, picolines, lutidines, and other pyrimidine bases, which contaminate the air in the production of tar and pitch[279]. The analysis of complex mixtures of polycyclic quinones in the atmosphere has been described[280].

VII. SUMMARY

Methods for the gas-chromatographic analysis of pollutants in the environment are being intensively developed. Among recently published studies, the following are noteworthy.

Sources of atmospheric pollution have been discussed[284], and the problems of analysis in the control of the pollution of the environment have been reviewed[285]. A detailed review of methods for the analysis of polluted air has been published[286]. Special reviews have recently been devoted to the gas-chromatographic analysis of air[287-289].

The general principles and methods of sampling air have been reviewed[290,291], and the criteria for evaluating methods for trapping traces of harmful substances in air on solid sorbents have been discussed[292]; active carbon[293] or polymeric sorbents[294] are most frequently used for this purpose. A promising sorbent is polyurethane foam, which has been found to be an effective material in traps for concentrating traces of phthalates[295], pesticides[296,297], polychlorobiphenyls[297], and PAH[298]. Polysorbimide-1[299] and the new carbon-containing sorbents Carbochrome-5 and Ambersorb XE-340[299,300] have proved to be very effective sorbents for micro-quantities of various chemical substances. Different types of apparatus and filters for trapping solid particles and aerosols have been described[301-303]. Selective sorbents for carbon monoxide have been found. These include silver-containing[304,305] and copper-containing[305] zeolites.

The electron-capture micro-detector, used in work with glass capillary columns, is being increasingly employed in the analysis of air[306]. The principles of the detection of traces of harmful substances in air using the COULD[307], conductometric[308], ultrasonic[309], and piezo-electric[310] detectors, the pyroelectric katharometer[311], and photometric[312] and electrochemical[313] detectors have been further developed. The combination of gas-chromatographic separation with detecting systems such as atomic-absorption[314] and atomic-fluorescence[315] spectrometers appears extremely promising for the analysis of micro-quantities of metals. The semiconducting detector[316] has an exceptionally high sensitivity towards organic substances with a large number of carbon atoms. A promising detector for the analysis of many inorganic compounds is the aerosol detector[317], and the neon ionisation detector can be used to determine approximately 10^{-5} vol.% of carbon monoxide in air without preliminary concentration[318]. A whole series of new methods based on reaction gas chromatography have been proposed for increasing the sensitivity of detection, and have been used to analyse air for micro-quantities of hydrogen fluoride[319], halogen compounds[320], styrene[321], carboxylic acids[322], and bischloromethyl ether[323]. The general principles of the chemical concentration of trace components using reaction gas chromatography has been described[324].

New versions have been developed for various methods of preparing standard mixtures of substances for calibrating detectors[325-327]; permeable polymer membranes are used particularly frequently for this purpose[328,329]. New methods of preparing effective glass capillary columns[330] and methods of using capillary columns for the highly sensitive quantitative analysis of micro-components[331] have been described. Micro-quantities of harmful substances in complex mixtures in polluted air are most frequently identified by the GC-MS method[332,333]. Other systems successfully used for this purpose include the microwave helium detector[334], a combination of gas chromatography with infrared and NMR spectroscopy[335], and the identification of the components of complex mixtures of hydrocarbons using the retention indices[336].

Gas chromatography has been used to analyse air for micro-quantities of phosgene[337], oxides of nitrogen[338], hydrogen cyanide[339], ozone[340], inorganic compounds of sulphur[341,342], carbon monoxide[343,344], the permanent gases[345], organometallic compounds[346], and metals in the form of chelate compounds[347]. Two recently published detailed reviews deal with the gas-chromatographic determination of metals, including the volatile complexes of metals with organic ligands[348,349].

A large number of papers have dealt with the determination of traces of organic substances in air. Methods for the analysis of hydrocarbons and other organic compounds

in solid dust particles and aerosols have been described[350-356]. Complex mixtures of atmospheric pollutants liberated from polymers and elastomers have been analysed[357,358] and the determination of a large number of organic substances in town and country air by GC-MS has been described[299,300]. Automobile exhaust gases contaminating the atmosphere have been analysed[359]. The gas-chromatographic method for determining traces of PAH in air has been further developed[360-362]; steel and glass capillary columns have been used to separate these carcinogenic substances. The analysis of air for phthalates[363], formic acid[364], phenols[365], acetone[366], acrolein and isoprene[367], biphenyl[368], peroxyacetyl nitrate[369], and various solvents[370] and odourants[371] has been described.

Gas chromatography has been used successfully for the analysis of amines[372], nitro-compounds[373], and the carcinogenic nitrosamines[374,375]. Odourants containing organic and inorganic compounds of sulphur[376-378], toxic low-molecular-weight chlorohydrocarbons[379-382], and very low concentrations of the carcinogenic vinyl chloride[383-385] and trichloroethylene[386] have been analysed. The ECD has been successfully used to analyse air for traces of pesticides[387,388], polychlorobiphenyls[389], and bischloromethyl ether[390].

A large number of automatic gas analysers have recently been developed for the operational control of the state of the atmosphere (in cities, industrial centres, factories, etc.), and the use of these analysers has been reviewed[391]. Gas-chromatographic analysers have been specially produced for analysing air for traces of carbon monoxide[392] and reactive hydrocarbons[393], for the analysis of solvent vapours[394], the determination of vinyl chloride[395], and the control of the concentration of sulphur dioxide[396], pesticide vapours[397], and bischloromethyl ether[398] in the atmosphere.

The present problems in the chemistry of the atmosphere and industrial hygiene relate chiefly to the accurate and sensitive determination of the concentration, in the troposphere, of hydrogen sulphide, sulphur dioxide, compounds of the halogens, and various acidic gases, and the identification and determination of a whole series of substances which irritate the eyes and have unpleasant odours. Gas chromatography, and particularly chromatographic–mass-spectral analysis with computer processing of the results, can obviously be of considerable assistance in the study of the qualitative composition of even very complex mixtures in polluted air, consisting of several hundred chemical compounds, and also for the accurate quantitative estimation of the level of contamination of air.

In recent years there has been a marked increase in interest in the standardisation of analytical methods for the study of polluted air[3]. It is now urgently necessary to unify methods for the analysis of photochemical oxidants, oxides of nitrogen, sulphur, and carbon, and solid particles suspended in air. The need to develop standard gas-chromatographic methods for the analysis of hydrocarbons in the atmosphere has been justified[281].

Methods of this kind have also been developed for other organic compounds[3,16,282,283].

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In conclusion it should be noted that gas chromatography has become the chief method for the analysis of polluted air, and it is now used to determine traces of practically all organic and many inorganic substances, and also metal aerosols and organometallic compounds entering the atmosphere. A whole series of problems remains unsolved in this field of the analysis of micro-components, however, associated with obtaining representative samples of the air, the concentrating of the trace components, the sensitive and specific detection of the substances being analysed against a background of interfering components, and also the reliable identification of trace components after chromatographic separation.

The solution of the problem of sampling air, which is essentially the problem of concentrating the trace components, depends to a large extent on the development of polymeric sorbents of the "Tenax" type, which make it possible to trap various chemical compounds effectively from contaminated air. On the other hand, a no less effective method involves the selective trapping of the trace components using reactive sorption columns placed in front of the trace component concentrator. This method of sampling appears more promising, since it facilitates considerably the subsequent identification of the substances being analysed and increases the speed of analysis. Methods of sampling (concentrating) trace components by bubbling the air through an active liquid also deserve attention.

Approximately ten selective and sensitive detectors (ECD, FPD, COULD, etc.) are used for the chromatographic analysis of trace components in air, but there is still no suitable detector for the selective detection of microquantities of inorganic substances (particularly carbon monoxide) against a background of the interfering organic trace components of the sample. The development of detectors selective towards the principal classes of atmospheric pollutant has made it necessary in some cases to detect only particular components (usually the most toxic) of the sample against a background of all other substances contaminating the air.

The most reliable information on the composition of complex mixtures of atmospheric pollutants is obtained by the GC-MS method, but the extensive application of this method is restricted by the high cost of the analyses. This has made it necessary to develop simpler methods for identifying trace components, based, for example, on the use of reaction gas chromatography or the chromatographic–distribution method of analysis.

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Artificial Light-sensitive Enzymatic Systems as Chemical Amplifiers of Weak Light Signals†

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The chemical principles of the amplification of weak light signals, based on photochemical and coupled chemical reactions, are examined. Systems where the dark amplification process is a catalytic reaction involving enzymes are discussed in greatest detail. Artificial enzymatic systems in which the level of catalytic activity can be varied under the influence of light is subjected to a critical analysis.
The bibliography includes 130 references.

CONTENTS

I.	Introduction	1027
II.	The idea of a chemical amplifier of weak light signals using enzymes	1028
III.	General principles of the construction of artificial light-sensitive enzymatic systems	1028
IV.	The use of artificial light-sensitive enzymatic systems in practical applications and in fundamental biochemical research	1035

I. INTRODUCTION

The reception of light signals constitutes the basis of a whole series of most important practical processes (ranging from photography to photoelectron multipliers) as well as unique natural phenomena such as vision, photosynthesis, phototaxis, etc. Usually (both in practical applications by man and in living nature) the primary received light signal is fairly weak and for its effective detection and utilisation it must be subjected to preliminary amplification in the receiving system.

Amplifiers are devices which amplify the transmitted power (in the given case the received light signal) by means of the energy of an extraneous source. Depending on the nature of this source, all amplifiers of light signals can be divided into physical (employing physical amplification principles, which are utilised, for example, in electronic devices)[1] and chemical (using chemical amplification principles, i.e. principles based on photochemical and coupled chemical reactions). In this review we shall consider only chemical amplifiers, because in the literature devoted to a general consideration of this problem unduly little attention has been given to such amplifiers.

The operation of any light-sensitive chemical system must include two stages: the absorption of light and the chemical reaction induced thereby. The amplification factor of a light signal in such a system can be naturally defined as the ratio of the number of molecules reacting

† Certain general aspects of this problem were discussed in our recent communication: K. Martinek and I. V. Berezin, Photochem. Photobiol., 29, 637 (1979).

under the influence of light (or the number of molecules of the reaction products formed) to the number of absorbed light quanta: the greater this quantity, the greater the light sensitivity of the system, i.e. the smaller the number of quanta which it can detect in principle. However, in conformity with the Stark–Einstein photochemical equivalence law, the yield of the primary photochemical reaction cannot be greater than unity. In this case the absorbed light quantum cannot give rise to more than one molecule of a chemical substance, so that the problem of the detection of a small number of light quanta is therefore transformed into the problem of the detection of a small number of molecules, which is just as difficult. Only a system where the primary intrinsic photochemical process is coupled to a subsequent "dark" process can therefore have a high amplification factor (i.e. an effective quantum yield exceeding unity). Ultimately the efficiency of the amplification will depend mainly on the nature of this secondary (dark) process. We shall examine certain examples.

Classical chemical amplifiers of light signals are silver halides suspended in gelatin gels, which are very widely used for the production of photographic images[2,3]. After absorbing a light quantum, the silver halide decomposes, giving rise to silver atoms, which play the role of catalysts of the subsequent dark development process. Another example of the chemical amplification of light signals is provided by the well known chain reactions induced by light[4]. The absorbed light quantum generates free radicals in the system, which then propagate the chemical chain growth stages (dark process).

In principle, the nature of the dark process which follows the primary photochemical reaction can be also non-chemical[2,3,5] (for example, in the "bubble" method based on the photochemical decomposition of azo-compounds with subsequent thermal expansion of nitrogen bubbles in a polymer film). However, the sensitivity (and sometimes also the resolving power) of the latter systems is low. Systems with a light-induced chain reaction, where the chain termination stages inevitably lead to a decrease of the amplification factor, suffer from the same disadvantage. On the whole, after analysing these and other examples[2,3,5], we concluded that one should regard as optimum from the standpoint of sensitivity systems with a *catalytic* dark process, which functions in accordance with the following general mechanism: catalyst molecules are generated under the influence of light, whereupon (in the dark reaction) they catalyse the chemical transformation of a substance present in the system (insensitive to light); in principle, the "turnover number" of a single catalyst molecule is unlimited (if it is possible to avoid the "poisoning" of the catalyst) and the amplification factor can therefore be as large as is required.

The principal and unfortunately evidently insurmountable disadvantage of silver halide catalytic system is that the world resources of silver are now being exhausted[5]. This makes it necessary to seek other, non-silver light-sensitive catalytic systems. There is no review in the literature dealing with the possibility of using biological catalysts for this purpose, but we believe that enzymes in fact give rise to excellent prospects in this field. Our confidence is based on the fact that, firstly, enzymes have a catalytic activity exceeding by many orders of magnitude that of the usual chemical catalysts[6] and, secondly, owing to their unique macromolecular structure, their action can be regulated in very fine detail, i.e. one can alter sharply and adequately the catalytic activity (and other processes) under the influence of even slight changes in the external medium[7]. On this basis, we put forward, justified, and applied experimentally the principle of the applification of light signals with the aid of light-sensitive enzymatic systems[8–10].

II. THE IDEA OF A CHEMICAL AMPLIFIER OF WEAK LIGHT SIGNALS USING ENZYMES

In order to elucidate the essential feature of the proposed approach, we shall consider a system containing a catalytically inactive derivative of an enzyme E_{inact} (which, however, is capable of being converted into an active catalyst E under the influence of light) and a substrate S of the given enzyme. When such a system is illuminated with light at the appropriate wavelength, the photochemical [reaction (1)] and dark [reaction (2)] reactions begin to take place in it:

$$E_{inact} \xrightarrow{light} E, \quad (1)$$

$$E + S \rightarrow E + P. \quad (2)$$

If theenzymatic reaction (2) obeys the Michaelis-Menten equation and the substrate concentration is sufficiently high to "saturate" the enzyme (see our previous publication[8]), the effective quantum yield Φ of the product is defined by the following expression[10]:

$$\Phi = \varphi k_{cat} t, \quad (3)$$

where k_{cat} is the catalytic rate constant for the enzymatic reaction (2) determined from the maximum rate of reaction and equal to the turnover number of the enzyme per unit time, φ is the quantum yield of the primary reaction (1), and t is the time of the dark enzymatic reaction. For the specified value of k_{cat} and in the presence of an inexhaustible supply of the substrate, the effective quantum yield Φ in such a system can evidently be as high as one wishes, since it is determined exclusively by the time of the dark reaction.

In practice the amplification of the light signal takes place as follows: if reaction (2) results in a coloured product P, then the "response" to a single light quantum (which cannot be actually perceived by the eye) is a number of the molecules of the coloured substance sufficiently large to be readily perceived even by the naked eye.

Eqn. (3) describes theoretically the functioning of light-sensitive enzymatic systems. However, for their experimental application, it is necessary to obtain specific derivatives of enzymes capable of changing their activity under the influence of light. Naturally, in principle one can use for this purpose light-sensitive proteins which already exist in living nature, such as, for example, the visual enzyme rhodopsin[11]. However, from the practical point of view, this procedure is quite unacceptable, because natural light-sensitive systems have an exceptionally detailed and complex organisation and are extremely unstable when isolated from their natural environment[12]. Consequently, the problem arises of synthesising artificial light-sensitive enzymatic systems, which is in fact the subject of this review.

III. GENERAL PRINCIPLES OF THE CONSTRUCTION OF ARTIFICIAL LIGHT-SENSITIVE ENZYMATIC SYSTEMS

It is logical to employ a chemo-bionic approach to the creation of artificial light-sensitive enzymatic systems[13]. After analysing photoregulatory processes *in vivo*,

Erlanger[14] concluded that the vast majority of the latter are based on the same principle: small light-sensitive molecules function as effectors (inhibitors, activators) in relation to the biologically active macromolecules, for example, enzymes (which are themselves as a rule insensitive to light). On illumination, the effector molecule is photochemically modified; this results in a change of the nature and (or) degree of its interaction with the biomacromolecule and ultimately the biological activity of the system changes. If this principle is used as the basis for the creation of artificial light-sensitive systems, then the entire vast arsenal of modern photochemistry can be used for this purpose[15,16]. In other words, one must examine suitable light-sensitive low-molecular-weight substances and select enzymes which interact with them. This is an extremely fruitful but laborious procedure, since it involves the selection of a specific light-senstitive effector–enzyme pair and there are no rules for such selection.

One can follow another approach, namely one can induce by means of light a direct change in the reactivity of either the substrate or the enzyme. The medium of the enzymatic reaction (or the microenvironment of the enzyme) can also be altered by the action of light.

The artifical enzymatic systems described in the literature, in which the level of catalytic activity can be altered under the action of light using the above principles, are subjected to a critical analysis below. Naturally, as regards applied aspects of the problem, a chemical amplifier of weak signals can be based only on systems where the light *initiates* (generates) catalytic activity. In practice a system will be regarded as being of this kind if its activity increases by 3–4 and more orders of magnitude after illumination. In other words, in practice one can use only systems where the primary photochemical process [a reaction of type (1)] can be represented in the following general form:

$$\text{System (enzyme + substrate + low-molecular-weight effector + medium) virtually without catalytic activity} \xrightarrow{\text{light}} \text{System with a high level of catalytic activity} \qquad (1a)$$

In such systems light acts either directly on the components of the enzymatic reaction (by altering the chemical or sorption properties of the enzyme itself, or the substrate, or, finally, the low-molecular-weight effector) or on the components of the medium (by altering, for example, the pH of the solution or the microenvironment of the enzyme molecule).

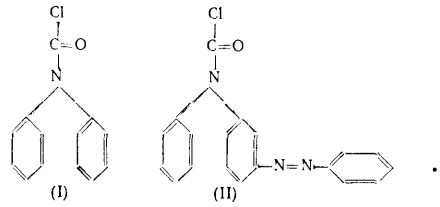
If the enzymatic activity of the system changes only within the range of 1–2 orders of magnitude under the influence of illumination, then such action of light is more correctly referred to as regulating. Despite the fact that the difference between these two types of enzymatic systems is only quantitative, we shall nevertheless consider them separately, bearing in mind the practical importance of the former. However, one must take into account the fact that in future studies only a slight modification of the method available hitherto (for example the replacement of one enzyme by another) can in principle alter sharply the quantitative characteristics of a particular system. Consequently a system which nowadays exhibits only weak regulatory effects, tomorrow (after it has been slightly modified) it can "begin to operate at full strength".

Fundamentally new possibilities for the regulation of catalytic activity have arisen from the use of immobilised enzymes (enzymes bound to a carrier)[17]. In this case sensitivity to an external stimulus can be "grafted" to the system via the carrier. This idea has already proved fruitful in the creation of sound-sensitive (mechano-sensitive) materials[18].

1. SYSTEMS WITH A LIGHT-SENSITIVE EFFECTOR

Regulation by Light of the Rates of Inactivation (or Reactivation) of Enzymes by their Interaction with Irreversible Photochromic Inhibitors

Diphenylcarbamoyl chloride (I) is a familiar irreversible inhibitor of α-chymotrypsin[19–21] and acetylcholinesterase[22]. Its photochromic azo-derivative, *N*-*p*-phenylazophenyl-*N*-phenylcarbamoyl chloride (II), can exist in the *cis*- and *trans*-configurations:



The equilibrium between these two forms can be displaced by illuminating (II) with light at a particular wavelength[13]:

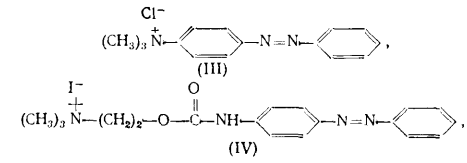
$$trans\text{-(II)} \underset{420\ nm}{\overset{320\ nm}{\rightleftharpoons}} cis\text{-(II)}\ . \qquad (4)$$

It was found[13] that *cis*-(II) inactivates chymotrypsin five times faster than *trans*-(II). Approximately the same differences between the rates of inactivation under the influence of the stereoisomers of (II) (as well as two other related azo-compounds) were noted also for acetylcholinesterase[23,24]. Thus, by illuminating the "enzyme + (II)" system with light having a greater or smaller wavelength, it is possible to alter the ratio of the inhibitor stereoisomers and thus regulate the rate of inactivation of the enzyme (and hence the catalytic activity of the system).

Chymotrypsin and acetylcholinesterase are inactivated under the influence of compounds of type (I) actually as a result of the carbamoylation of the active centre. The carbamoyl derivative of acetylcholinesterase can be reactivated by prolonged incubation at alkaline pH values, and for the *cis*- and *trans*-stereoisomers of inhibitor (II) slightly different rates of reactivation of the "inhibited" enzyme were found[23]. This made it possible to regulate with the aid of light also the rate of this stage of the enzyme–inhibitor interaction.

Regulation of Enzyme Activity by Light with the Aid of Light-sensitive Reversible Inhibitors

The *cis–trans* stereophotoisomerisation of azo-compounds has also been used[23,25] for the reversible regulation of the catalytic activity of acetylcholinesterase. *N*-*p*-Phenylazophenyltrimethylammonium chloride (III) and *N*-*p*-phenylazophenylcarbamoylcholineiodide (IV),

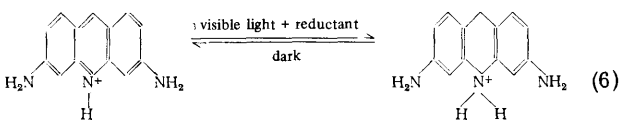


which are competitive inhibitors of this enzyme, exist in the *cis*- and *trans*-forms capable of photochemical interconversions, for example[25]:

$$\textit{trans}\text{-(IV)} \underset{\text{dark}}{\overset{\text{light (348 nm)}}{\rightleftharpoons}} \textit{cis}\text{-(IV)} \quad . \tag{5}$$

The inhibition constants for the *trans*- and *cis*-isomers of (IV) are 1.6 and 3.6 μmole litre^{-1} respectively[25]; the difference is due[26] to the specific structure of the active centre of acetylcholinesterase. Using the differences between the binding capacities of the stereoisomers in relation to the active centres, it is possible (by switching light on and off) to alter reversibly the degree of inhibition of the enzyme and hence the level of the catalytic activity of the system.

We used another photochemical reaction for the reversible regulation of the catalytic activity of α-chymotrypsin. Proflavin (3,6-diaminoacridine), which is a competitive inhibitor of this enzyme[27,28], is capable of being reduced photochemically under the action of visible light in the presence of an organic reductant with formation of 3,6-diaminoacridan: the latter is reoxidised in the dark to proflavin[29]:



(6)

We have shown[30] that, in the course of its photochemical reduction, the ability of proflavin to inhibit α-chymotrypsin disappears (probably as a result of the breakdown of the planar structure of the molecule because the $C_{(9)}$-atom becomes tetrahedral). Consequently, when the "α-chymotrypsin + proflavin + reductant (ascorbic acid)" system is illuminated, the level of its catalytic activity increases (because the inhibitor is inactivated), while in the dark it decreases again.

Regulation by Light of the Potential Difference across a Biological Membrane with the Aid of Photochromic Effectors

The potential difference across certain biomembranes, whose composition includes acetylcholinesterase, diminishes (the membrane depolarises) in the presence of agents interacting specifically with the enzyme (such as acetylcholine or carbamoylcholine)[31–33]. This fact has been used[34,35] for the creation of a system for the photoregulation of the membrane potential using both irreversible[13,23,24] and reversible[23,25] photochromic inhibitors of acetylcholinesterase: under the influence of light, it is possible to alter the ratio of the *cis*- and *trans*-isomers of the inhibitor and hence (bearing in mind their different reactivities in relation to the enzyme) the degree of inhibition of acetylcholinesterase. It was found[34,35] that the membrane potential of the electric organ of the ray can be regulated in this way.

Thus, in systems with light-sensitive effectors, examined above, it is indeed possible to regulate the level of catalytic activity within fairly wide limits. However, this is clearly insufficient for the creation of chemical amplifiers of weak signals. As already mentioned [see Eqn. (1*a*)], it is in fact necessary to *initiate* catalytic activity by the action of light; this can be achieved if the photochemical reaction results in the appearance in the system of an effector (for example, an activator or a cofactor) without which the enzyme is in principle incapable of catalysis.

Initiation by Light of the Catalytic Activity of Haem-containing Enzymes

The active centre of the majority of haem-containing oxidation enzymes includes bivalent iron. For example, peroxidase is an enzyme whose globule contains, apart from the protein component, a prosthepic group (haemin), consisting of a complex of an iron ion and protoporphyrin. Neither apoperoxidase, which contains no haemin, nor haemin, nor the complex of apoperoxidase with protoporphyrin have any appreciable enzyme activity.

The principle of initiating activity by light in such systems has been developed in our laboratory[36]. One takes a mixture of apoperoxidase, protoporphyrin, and a complex iron salt [for example, potassium oxalatoferrate(III)], which does not interact with protoporphyrin; such a system should evidently have no catalytic activity. After illumination of the complex iron salt, the iron ion is liberated[37,38]:

$$\text{potassium oxalatoferrate(III)} \xrightarrow{\text{visible light}} Fe^{2+}, \tag{7}$$

and this is followed by complex formation processes:

$$\text{protoporphyrin} + Fe^{2+} \rightarrow \text{ferroprotoporphyrin} \xrightarrow{O_2} \text{haemin}, \tag{8}$$

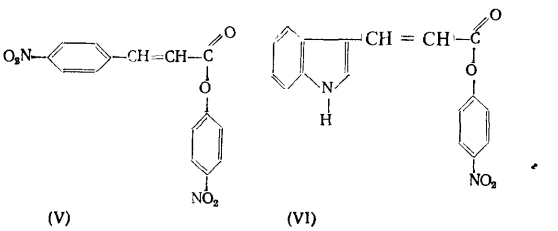
$$\text{apoenzyme} + \text{haemin} \rightarrow \text{peroxidase}. \tag{9}$$

Thus an active enzyme can be "constructed" as a result of the primary photochemical process (7) and the subsequent dark reactions (8) and (9).

2. SYSTEMS WITH A LIGHT-SENSITIVE SUBSTRATE (OR QUASI-SUBSTRATE)

Regulation by Light of the Rates of Reaction of Enzymes with Synthetic Substrates Capable of Photoisomerisation

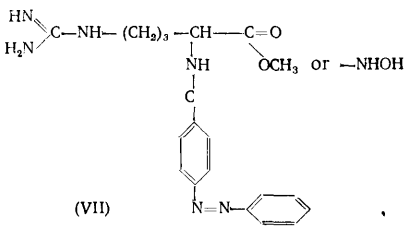
(a) The esters of β-arylacrylic acids can be regarded as structural analogues of specific α-chymotrypsin substrates[39]. The second-order rate constants for their hydrolysis by α-chymotrypsin are much higher for the *trans*-stereoisomers than for the *cis*-stereoisomers: by a factor of 5×10^3 for *p*-nitrophenyl esters of *p*-nitrocinnamic acid (V) [40] and by a factor of 10^3 for the *p*-nitrophenyl esters of indolylacrylic acid (VI) [41]:



(V) (VI)

Consequently, by illuminating a mixture of the enzyme and the *cis*-isomer of the substrate, it is possible to accelerate the enzymatic process greatly[40].

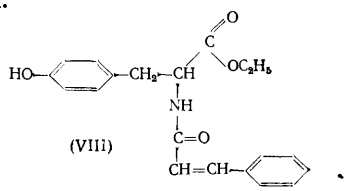
(b) Amides and esters of *N*-α-benzoyl-L-arginine — classical low-molecular-weight substrates of trypsin[42–44]. The stereoisomers of their azo-derivatives (VII).



(VII)

The methyl ester and hydroxamide of *N*-**α**-*p*-phenylazophenyl-L-arginine differ severalfold in reactivity towards trypsin[45]. Under the influence of light at different wavelengths, the *cis*- and *trans*-stereoisomers of (VII) are interconverted. Consequently, with the aid of light, one can, as it were, "switch over" the rate of enzymatic reaction from one value to another[45].

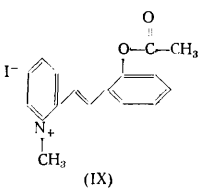
(c) When the reaction involving the photostereoisomerisation with respect to the C = C bond was used, it was possible[46] to regulate with the aid of light the rate of the chymotrypsin hydrolysis of the ethyl ester of *N*-α-cinnamoyl-L-tyrosin:



(VIII)

Compound (VIII) can be regarded as an analogue of the ethyl ester of *N*-acetyl-L-tyrosine, which is a classical specific substrate of α-chymotrypsin[39].

(d) The rates of hydrolysis of compounds of type (IX)



(IX)

catalysed by butyrylcholinesterase, differ severalfold for the *cis*-*trans*-stereoisomers[47]. Consequently, using the photostereoisomerisation of a substrate of type (IX), it is possible to regulate the rate of the enzymatic reaction. The authors[47] suggest that the rate-limiting stage in the enzymatic hydrolysis is the desorption of the product molecule (the corresponding alcohol) from the active centre. This hypothesis is extremely likely, because it is known that product molecules can be desorbed from enzyme macromolecules at a fairly low rate[48,49].

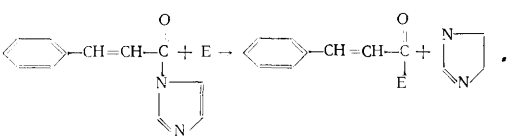
Reactions of Enzymes with Photoexcited Substrates

Molecules in photoexcited states differ sharply in their chemical properties from those in the ground state (it is therefore possible to investigate their reactions despite the extremely low steady-state concentration of the excited molecules)[59]. Consequently, in principle, one may expect that the reaction of the enzyme with the photoexcited substrate can have a different rate than that with the non-excited substrate. The foregoing may have a bearing on the surprising results obtained by Comorosan and coworkers[51–54], who showed that, when low-molecular-weight substrates of various enzymes are irradiated with low doses of ultraviolet light, long-lived excited states are formed and the rates of their reactions with enzymes can be several times higher than those observed with the non-excited substrates. This effect depends greatly on the irradiation conditions, but the mechanism of the phenomenon remains obscure.

Thus, with the aid of light-sensitive substrates it is also possible (as for light-sensitive effectors) not only to regulate the rate of the enzymatic reaction but actually to initiate the latter [this has been shown[40] in relation to compounds of type (V)]. However, the foregoing factors are insufficient for the creation of a chemical amplifier of weak signals— instead of initiating the reaction (by activating the substrate), the catalytic activity of the system must be stimulated. This can be achieved by employing "quasi-substrates", whose chemical reaction at the active centre proceeds via relatively unreactive (unstable) intermediate compounds. As a result of such "chemical modification of the active centre" by the quasi-substrate, the catalyst is, as it were, "poisoned". Using such stable and catalytically inactive "enzyme derivative" (modified by the quasi-substrate at the active centre), one can attempt to alter (increase) the enzyme reactivity under the influence of light and thereby regenerate the free active centre.

Initiation by Light of the Catalytic Activity of Enzymes with the Aid of Photochromic Quasi-substrates

(a) The possibility of initiating by light the catalytic activity of artificial enzymatic systems was demonstrated for the first time at Moscow University[8–10]. The principle of the effect is as follows. It is known[39] that acylation of the hydroxyl in the serine residues in the active centre of α-chymotrypsin (a protolytic enzyme) leads to complete inactivation of this biocatalyst. Deacylation of the resulting acylenzyme leads in its turn to the complete regeneration of the catalytic activity. Taking these factors into account, the active centre of α-chymotrypsin has been acylated[8,9] by *cis*-cinnamoylimidazole (the *trans*-stereoisomer of this reagent is a familiar titrant of α-chymotrypsin[55]):



(10)

(X)

The *cis*-cinnamoyl-α-chymotrypsin (X) formed in this process is an extremely stable acylenzyme: even at the pH optimum the deacylation rate constant is 4×10^{-4} min^{-1}, i.e. the half-deacylation time is more than 24 h. (By altering the pH away from the optimum, it is possible to increase this time still further). On illumination with ultraviolet light, the *trans*-stereoisomer is formed from the *cis*-acylenzyme, and is extremely rapidly deacylated (the half-reaction time is ~1 min). The observed difference between the reactivities of the *cis*- and *trans*-stereoisomers of the acylenzymes (by a factor of 2000) can be increased still further by introducing the nitro-group in the *para*-position of the aromatic ring in the cinnamoyl group. In this case the *trans*-acylenzyme is deacylated 2.5×10^4 times faster than the corresponding *cis*-acylenzyme[10]. The causes of the *trans*-specificity of α-chymotrypsin have been discussed[41,56]. The *cis*- and *trans*-cinnamoyl derivatives of another protolytic enzyme (trypsin) show a still greater difference in reactivity[57,58].

A chemical amplifier of weak light signals can be constructed in the following form using the systems described. We shall use, for example, *cis*-cinnamoylchymotrypsin, which is itself catalytically inactive (Fig. 1*a*) and is hardly deacylated under the experimental conditions[8,9]. If such a system is irradiated with ultraviolet light, the acylenzyme undergoes *cis-trans* photostereoisomerisation and the resulting *trans*-acylenzyme hydrolyses rapidly:

$$cis\text{-(X)} \xrightarrow{\text{light}} trans\text{-(X)} \xrightarrow{H_2O} \text{enzyme} + trans\text{-cinnamic acid.} \quad (11)$$

The kinetics of these processes can be followed on the oscillogram obtained in the flash-induced hydrolysis of *cis*-nitrocinnamoylchymotrypsin[59] (Fig. 2). Eqn. (11) shows that illumination results in the regeneration of catalytic activity (see Fig. 1*b*) and a coloured product, for example, will therefore begin to be formed in the presence of the substrate [Eqn. (2)]. The effect quantum yield Φ of the product **P** (the amplification factor for the light signal) in the system can be estimated by Eqn. (3) assuming that the quantum yield of the *cis-trans* stereoisomerisation is $\varphi = 0.3$ (at 313 nm) [56] and the catalytic constant for a specific substrate at the pH optimum for the activity of chymotrypsin is $k_{cat} \simeq 100\ s^{-1}$.[39] If the time of the dark reaction t is, for example, 1 h, then, according to Eqn. (3), $\Phi = 0.3 \times 200 \times 3600 \simeq 2 \times 10^5$, i.e. more than 10^5 product molecules are produced in the system during this period for one absorbed light quantum.

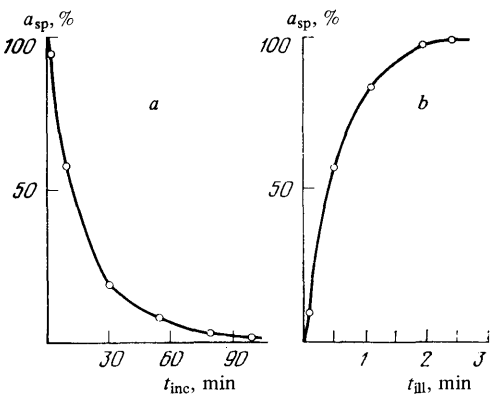


Figure 1. Variation of the specific catalytic activity (a_{sp}) of chymotrypsin incubated with *p*-nitrophenyl *cis*-4-nitrocinnamate (curve *a*; t_{inc} is the incubation time) and on subsequent illumination of the resulting acylenzyme—*cis*-4-nitrocinnamoylchymotrypsin (curve *b*; t_{ill} is the illumination time)[8,10].

Thus it is seen that the systems described are extremely sensitive light detectors (see Kazanskaya's review[60]).

(b) Another principle has been formulated in studies[61,62] where a photochemical method was proposed for the investigation of the aminoacid environment of the active centre of the enzyme. For the reaction of α-chymotrypsin with *p*-nitrophenyl diazoacetate—an analogue of *p*-nitrophenyl acetate which is a classical non-specific substrate of proteases[63]—the product is a diazoacetylenzyme—an extremely stable acylenzyme without catalytic activity.

For example, diazoacetyl-α-chymotrypsin is hardly deacylated in the course of 48 h (at pH 6.5) [44], while acetyl-α-chymotrypsin is rapidly deacylated under these conditions. The difference is associated with the diminution, as a result of conjugation with the diazo-group, of the electrophilic properties of the carbonyl carbon atom in the substrate residue. On illumination of diazoacetyl-α-chymotrypsin with ultraviolet light, nitrogen is split off[61] from the diazoacetyl residue with formation of a carbene radical. This radical hydrolyses and the resulting hydroxyacetyl-α-chymotrypsin is rapidly deacylated with regeneration of enzyme activity:

$$\text{E}-\overset{\overset{O}{\|}}{C}-CH_2-\overset{+}{N}\equiv N \xrightarrow[H_2O]{\text{u.v.light}} \text{E}-\overset{\overset{O}{\|}}{C}-CH_2-OH + N_2 \rightarrow \text{E} + HOCH_2COOH \quad . \quad (12)$$

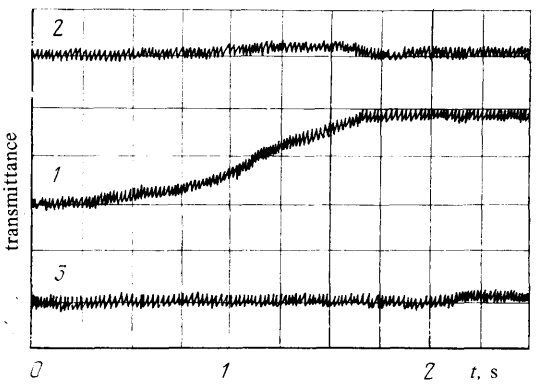


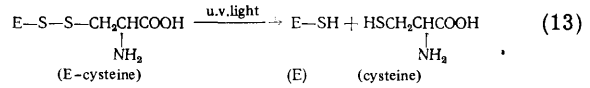
Figure 2. The oscillogram (curve *1*) of the change in the transmittance (320–360 nm) of a solution of *cis*-4-nitrocinnamoylchymotrypsin as a result of pulse irradiation (10^{-4} s) at time $t = 0$. Curves *2* and *3* correspond to 0 and 100% transmittance[59].

3. THE ACTION OF LIGHT ON THE ENZYME (INCLUDING A MODIFIED ENZYME)

Activation by Light of Catalytically Inactive Enzyme Derivatives (Modified at the Active Centre)

The principle of the approach is that the enzyme is modified initially with formation of a catalytically inactive derivative $E_{\mathbf{inact}}$ [see Eqn. (1)] and then the modifying agent (or its influence) is removed with the aid of light. A fairly convenient object for studies of this kind is the sulphydryl protolytic enzyme papain. The sulphydryl group of cysteine, which forms part of the active centre of the enzyme, plays the most important role in the catalytic function of papain[64]. However, the enzyme is usually in the inactive form, where the sulphydryl group of the active centre forms a mixed disulphide with an additional cysteine residue (papain–S–S-cysteine)[65,66]; for the catalytic activity to be shown by papain, the latter must be activated, for example, chemically (in this activation the S–S bond of the disulphide is cleaved).

In principle, disulphide bonds both in peptides and in proteins can be cleaved not only chemically but also photochemically[67-69]. This approach has been used[70] for the photochemical activation of papain: on illumination with ultraviolet light of a solution containing papain–S–S-cysteine, a catalytically active enzyme is formed:



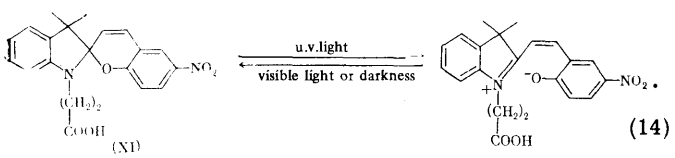
(13)

This principle was developed further in our laboratory[71]. As a result of the oxidation of active papain catalysed by copper ions, a disulphide dimer of the enzyme, namely papain–S–S–papain, was obtained. On illumination of the dimer with ultraviolet light, the disulphide bond is cleaved with formation of two molecules of the catalytically active enzyme. The quantum yields of the photoactivation process are in both cases in the range 0.1–1.0.

Regulation by Light of the Catalytic Activity of Enzymes with the Aid of Photochromic Effectors Attached to the Protein Globule outside the Active Centre

When photochromic polymers are illuminated[72,73], one may expect a change in their structure. This effect has been observed experimentally[74-79]. In the above studies azo-dyes [for example compounds of type (II)–(IV)] were attached covalently or non-covalently to synthetic polymers or proteins. The *trans*-configuration of the dye is thermodynamically more stable but *trans–cis* stereoisomerisation takes place on illumination. It has been shown[74-76] that such photochemical reaction does indeed induce a considerable change in the polymer structure (revealed, for example, by a change in the viscosity of its solutions).

Enzyme macromolecules exhibit a biological activity which is extremely sensitive to the conformation of the protein globule[7]. From this point of view, it is of interest to modify the enzyme by photochromic reagents (but not at the active centre, in order to retain the catalytic activity) and to investigate the dependence of the activity of the biocatalyst on the light-regulated structure of the modifying agent. This idea has been realised experimentally[80]. A spiropyran (XI), widely used to produce photochromic polymers, served as the modifying agent for α-amylase[72,73]. On illumination with ultraviolet light, compound (XI) isomerises:



(14)

The isomerisation can be reversed by illumination with visible light or in the dark[15,81].

Namba and Suzuki[80] obtained the anhydride of compound (XI), which was then used to modify the amino-groups of α-amylase molecules. When the enzyme modified in this way is illuminated with ultraviolet light, its catalytic activity falls, while in the dark the enzyme is reactivated.

The mechanism of the regulation of systems described in this section is based on the fact that the molecular structure of the modifying agent changes under the influence of light. In principle, the mechanism of the regulation of the catalytic activity of the enzyme modified outside the active centre can also be different. The Change in the Conformational-Solvation state of the Enzyme Induced by Light. The protein molecules of enzymes contain a number of intrinsic chromophores (for example, aromatic aminoacid residues) capable of absorbing light effectively. In some cases such light absorption can activate the biocatalyst. Thus illumination of a solution of aldolase with ultraviolet light leads to a prolonged reversible increase of its enzymatic activity[82,83]. An analogous effect, but this time following the illumination of aldolase in the presence of a substrate, was observed by Volotovskii et al.[84], who proposed an interesting explanation of this effect: when light is absorbed by tryptophan residues, a radiationless dissipation of excitation energy in the form of heat can occur, in particular, in the enzyme–substrate complex, which can lead to the breakdown of the structure of water in the solvation shell of the macromolecule. This facilitates, in its turn, the allosteric conformational transition in the enzyme subunits, which leads to the formation of an aldolase conformation with an enhanced catalytic activity.

Other data[85,86] agree with this hypothesis. The difference between these results and those of the above studies[82-84] consists in the fact that the primary light acceptors were not the intrinsic chromophores of the protein but residues of diazotised *p*-aminobenzoic acid covalently attached to the sulphydryl groups of aldolase (in this case the protein absorbs visible light). Evidently such modification should not be reflected significantly in a change of the properties of the enzyme according to the mechanism of Volotovskii et al.[84] Indeed, when the modified aldolase is illuminated, its conformation changes (this can be followed from the change in the absorption spectra and the electrophoretic mobility)[86] and the kinetics of the cleavage of fructose-1,6-diphosphate catalysed by this enzyme are also altered[85]. Apparently the mechanism proposed[84] can be fairly general for different enzymes.

Another mechanism (one cannot rule out the possibility that it is to some extent similar to that already described) of the increase of the activity of enzymes under the influence of light may be proposed on the basis of Fröhlich's hypothesis[87,88], according to which biological objects, particularly proteins, can exist in long-lived excited states. In the case of enzymes the catalytic activity of these states may be different from that of the ground states; the transition from the ground to the excited state can be induced, for example, by light. An experimental study of this kind has been carried out[89], in which it has been shown that, when chymotrypsin is irradiated with a laser beam (457.9 nm), its activity increases appreciably. According to the authors[89], the picture outlined by Fröhlich actually obtains in this instance.

Photoinactivation of Enzymes

In principle, the familiar phenomenon of the photoinactivation of enzymes can be used to create light-sensitive enzymatic systems. The first study[90] devoted to this problem was published as early as 1879 and by now hundreds of such investigations have been made. We shall therefore merely refer to the most exhaustive reviews[91-97].

Inactivation under the influence of ultraviolet light is due to the photodegradation of the aminoacid residues of the protein globule (in the first place, tryptophan and cysteine residues). The photoinactivation quantum yield is in this case 0.001–0.1 and depends on the nature of the enzyme, its conformation, and the conditions in the medium. Certain flavin enzymes are inactivated under the influence of visible (blue) light. Here the cofactor (flavin

mononucleotide) plays the role of a sensitiser of the apoenzyme degradation process[98].

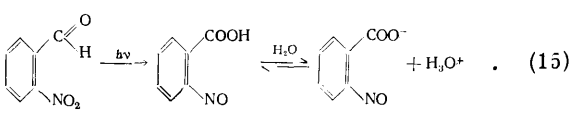
The so-called photodynamic effect, i.e. the photochemical oxidation of protein molecules sensitised by dyes, is also well known[99]. The mechanism of this effect consists in the transfer of molecular oxygen dissolved in water to the protein via the formation of an intermediate adduct of the triplet-excited dye molecule and oxygen. The photodynamic effect occurs when protein solutions are irradiated with visible light in the presence of various dyes (eosin, Methylene Blue, etc.); the enzyme photoinactivation quantum yields are usually in the range 0.001–0.1.[99]

4. THE CHANGE IN THE MEDIUM OF THE ENZYMATIC REACTION UNDER THE INFLUENCE OF LIGHT

The Light-Induced Jump in pH

Almost all enzymatic reactions are extremely sensitive to the pH of the solution: their rates decrease sharply when the pH deviates from the optimum value[6]. This factor led to the idea that the rates of enzymatic reactions can be regulated by a photoinduced change in the pH of the medium[100]. Photochemical reactions which lead to the formation of strong acids or bases have been described in the literature. We shall quote some examples of such reactions.

(a) When a solution of *o*-nitrobenzaldehyde is irradiated (436 nm), a phototautomerisation reaction takes place: *o*-nitrobenzaldehyde is converted into *o*-nitrobenzoic acid with a quantum yield $\varphi = 0.5$ (see Terenin[15], p.211):



(15)

When reaction (15) is carried out in aqueous solution, the resulting acid dissociates with formation of a hydronium ion, i.e. in this case illumination leads to a decrease of the pH of the medium.

(b) When complex transition metal (CO^{3+}, Cr^{3+}, etc.) ammines are irradiated with visible light, a photoaquation reaction takes place (with quantum yields of 0.01–1.0),[101,102] for example:

$$[CO(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{h\nu} [Co(NH_3)_4(H_2O)Cl]^{2+} + NH_3 . \quad (16)$$

The ammonia formed as a result of reaction (16) reacts with water (i.e. with the reaction medium).

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-,$$

which leads to an increase in the alkalinity of the solution.

(c) Transition metal (Fe^{3+}, Co^{3+}) oxalates undergo a photochemical oxidation-reduction reaction with a quantum yield of approximately unity on illumination with visible light (this process constitutes the basis of the action of the oxalatoferrate (III) actinometer[37,38]), for example:

$$2Fe(C_2O_4)_3^{3-} \xrightarrow{h\nu} 2Fe(C_2O_4)_2^{2-} + C_2O_4^{2-} + 2CO_2. \quad (17)$$

The carbon dioxide formed in this process reacts with water:

$$CO_2 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-,$$

which leads to an increase in the acidity of the medium.

Naturally the systems (a)–(c) enumerated above do not exhaust the photochemical reactions accompanied by a change in the pH of the medium.

Consider an enzyme and a substrate at a pH such that the rate of the enzymatic reaction is negligibly small. We then add one of the above reagents, for example, *o*-nitrobenzaldehyde [Eqn. (15)] or chloropentamminecobalt [reaction (16)]. If such a system is now illuminated, the pH of the solution changes and if the change is directed towards the pH optimum for the enzyme activity, the rate of the enzymatic reaction increases.

The above principle[100] was tested in relation to photoinitiated reactions catalysed by α-chymotrypsin [using system (a)][46] and trypsin [system (b)].[103]

Photoregulation of the Rates of Enzymatic Reactions as a Result of the Change in the Microenvironment of the Enzyme under the Influence of Light

New possibilities for the regulation of the catalytic activity by light arose when the enzyme was incorporated in a polymer film (membrane) containing a photochromic effector. Such an effector can be either introduced mechanically into the polymer carrier or can be attached covalently.

(a) Chymotrypsin and azobenzene were incorporated mechanically in an octanol/water membrane stabilised with sodium stearate[104]. Azobenzene does not interact with the enzyme, but the change in its structure as a result of the *cis–trans* photostereoisomerisation induces structural changes also in the membrane, which influences the catalytic activity of chymotrypsin (apparently as a result of the effect of the microenvironment).

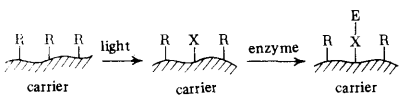
(b) An interesting idea for the photocontrol of enzymatic processes has been described in studies[105,106] where the amino-groups of collagen were modified by a photochromic compound [the anhydride of compound (XI)]. Films containing non-covalently incorporated enzymes—urease[105] or lactate dehydrogenase[106]— were then obtained from such collagen. When immobilised enzyme systems of this kind are illuminated, the structure of the modified polymer changes and hence also the microenvironment of the enzyme, which reduces the catalytic activity of the system. After the system has been kept in the dark, the photochemical reaction is reversed [in conformity with Eqn. (14)] and the activity of the enzymes rises to the initial level.

5. SYSTEMS WITH A CARRIER IN WHICH LIGHT INITIATES ENZYME IMMOBILISATION CENTRES

In virtually all the examples examined above (sub-sections 1–4) the presence of light sensitivity was indisolubly linked to a specific enzyme system. In other words, each mechanism whereby it was possible to "graft" light sensitivity artificially onto the system depends strongly either on the structure of the active centre, or on the nature of its interaction with low-molecular-weight ligands, or on the degree of its "response" both to changes in the structure of extremely remote regions of the protein globule and to changes in the reactivity of the medium, etc. Consequently the method developed for one enzyme cannot be automatically used in another system.

In order to overcome this disadvantage, we propose a fundamentally new, universal method based on the use of a carrier for the immobilisation of the enzyme. The basic

idea of this method is reflected in the following scheme:



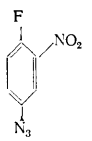
(1b)

The functional groups R of the initial carrier do not interact with the enzyme. Under the influence of light, they are transformed chemically (R — X) with formation of functional groups X capable of interacting with the enzyme either chemically or via a sorption process. Thus the enzyme is attached to the regions of the carrier surface exposed to light, while it is absent from the non-illuminated sections. The attached enzyme can be made visible by treating the system with a substrate giving rise to coloured products as a result of the enzymatic reaction.

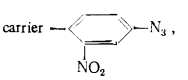
An evident advantage of this approach is that it is applicable to virtually any enzyme (because the molecules of all enzymes consist of the same aminoacid residues). Furthermore, methods for the immobilisation of enzymes on carriers have now been developed in extremely great detail[107-109]. We shall therefore indicate only photochemical methods whereby the ability to bind an enzyme can be "grafted" onto a carrier.

Photochemical Modification of the Functional Groups of the Carrier

(a) The immobilisation of aspartase with the aid of the photochemical Knowles reagent[112] [4-azido-1-fluoro-2-nitrobenzene (XII)] has been described[110,111]. This reagent was added to a carrier, namely to alkylamino-glass, in order to immobilise enzymes. As a result of the substitution of fluorine by the nucleophilic NH_2 groups of the carrier, compound (XIII) was formed:



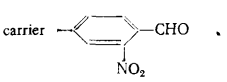
(XII)



(XIII)

which is capable of splitting off nitrogen under the influence of light with formation of an extremely reactive nitrene radical. If the illumination is carried out in the presence of an enzyme, then at the sites exposed to light the enzyme is bound covalently to the modified carrier (XIII) by interacting with the nitrene, the prospects for this approach in the photoimmobilisation of enzymes have been very fully described by Guire[111].

(b) Another method was proposed by ourselves[128]. In an optically transparent polymer carrier, containing *o*-nitrobenzaldehyde groups (XIV), the photochemical reaction (15) should proceed with formation of carboxy-groups:

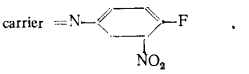


(XIV)

The remaining aldehyde groups (in the non-illuminated regions) must be blocked by an amine and the existing carboxy-groups (at the illuminated sites) must be activated, for example, by carbodiimide and the enzyme must be grafted to them (by a standard method[107-109]).

Photochemical Addition to the Carrier of Functional Groups Capable of Interacting with Enzymes

The photochemical immobilisation of enzymes using the Knowles reagent (XII) can be achieved in two ways (see the discussion of this problem by Guire[111]): either by attaching (XII) to the carrier with the aid of a nucleophilic substitution reaction involving the aromatic ring (see above) or by illuminating a mixture of (XII) and a carrier without nucleophilic groups. In the latter case the reactive nitrene radical formed at the illuminated sites is attached covalently to the carrier with formation of compound (XV):



(XV)

If an enzyme solution is then added, the amino-groups of the protein react with the fluoronitrophenyl residue (nucleophilic substitution of fluorine) in compound (XV), which leads to covalent immobilisation of the biocatalyst. In order to increase the rate of the last reaction, the Knowles reagent can be replaced by its more reactive derivative[113], a whole series of which have been synthesised by Guire[114].

Photochemical Formation of a Carrier

We used the photogel-formation process for the photoimmobilisation of enzymes[115]. For example, the classical polyacrylamide gel for the immobilisation of enzymes[116] and other polyacrylate gels can be obtained by illuminating solutions of the corresponding monomers with visible light in the presence of the dye riboflavin[117] or by illuminating with ultraviolet light[118]. Thus, when a thin layer of a solution of monomers is deposited on a plate the illuminated, a gel, retained on the plate, is formed at the illuminated sites, at the non-illuminated sites the monomer solution can be readily washed off with water. The enzyme is retained in the carrier mechanically (when it is added beforehand to the polymerisation mixture)[118] or it can be "grafted" chemically after polymerisation to the gel already formed[115].

An important feature of the methods which we proposed[115] consists in the fact that the light-initiated radical polymerisation processes are characterised (by virtue of the chain mechanism) by high quantum yields, greatly exceeding unity. This implies that one light quantum can ensure, in principle, the immobilisation of more than one enzyme molecule. This leads to additional possibilities [apart from the coupled enzymatic reaction — see Eqn. (2)] for the amplification of the light signal.

IV. THE USE OF ARTIFICIAL LIGHT-SENSITIVE ENZYMATIC SYSTEMS IN PRACTICAL APPLICATIONS AND IN FUNDAMENTAL BIOCHEMICAL RESEARCH

Analysis of literature data combined with the new approaches which we proposed shows that catalytic activity in an enzyme system can be indeed "induced" by artificial means [via mechanisms (1a) or (1b)]. In conclusion we shall note the following three factors.

(1) There is no doubt that extremely effective amplifiers of weak light signals, including new non-silver photographic processes (see the relevant reviews[60,129,130]), will be created in the immediate future on the basis of artificial

light-sensitive enzymatic systems. The success of future research will depend on the following two characteristics of the enzymatic system employed: the amplification factor and the spectral sensitivity.

(a) As already mentioned above [see the discussion of Eqn. (3)], the effective quantum yield in light-sensitive enzyme systems is extremely high. Furthermore, there exist at least two ways of increasing it further.

In the first procedure the activation of the corresponding zymogen is used as the first of the dark reactions (2) (zymogens are catalytically inactive natural enzyme precursors capable of enzymatic activation). For example, trypsinogen has no enzyme activity, but is converted into an active enzyme under the influence of trypsin[119]. This process is autocatalytic: in principle, even one trypsin molecule can activate the entire available "store" of the zymogen. Consequently, trypsinogen is extremely sensitive to even very small concentrations of trypsin. Hence the idea of creating the following light-sensitive enzymatic system naturally arises: a catalytically inactive, but capable of being activated by light, trypsin derivative + trypsinogen + trypsin substrate. When such a system is illuminated, the active enzyme is formed from the inactive trypsin derivative and activates the zymogen, while the product of the activation process hydrolyses the substrate. Evidently in this case the trypsin formed under the influence of light as it were "multiplies" due to the activation of the zymogen, which leads to a transition from a linear dependence of the effective quantum yield on the dark reaction time [Eqn. (3)] to an exponential dependence[120] and this ensures increased primary light signal amplification factors; see also Refs. 57, 58, and 103 and a review[60].

In the second procedure the photochemical formation of the carrier ensures the possibility of immobilising more than one enzyme molecule with the aid of a single light quantum[115] (see Section III.5).

(b) As regards the second important characteristic of the light-sensitive enzymatic system, namely its spectral sensitivity, the latter can be altered by varying the molecular structure of light-sensitive low-molecular-weight components, i.e. the substrate (see, for example, Varfolomeev and coworkers[10,56]) or of the effector for the enzymatic reaction or, finally, of the enzyme modifying agent.

New possibilities arise from the use of sensitised photochemical reactions, because in this case it is sufficient to vary the molecular structure (and hence the spectral sensitivity) of the sensitiser. So far it has not been possible to find a sensitiser of photochemical reactions occurring directly in the active centre of the enzyme[121], which is apparently associated with the extremely complex organisation of the active centre, i.e. with different kinds of steric hindrance. The photopolymerisation process which results in the formation of a carrier for the subsequent immobilisation of enzymes is therefore extremely promising[115]. It is significant that photopolymerisation processes do not impose unduly drastic limitations on the structure of the sensitiser molecule[122].

(2) The approaches examined in the present review to the regulation under the influence of light of the rates of enzymatic reactions should find applications also in fundamental enzymological research. Particularly wide prospects arise in photochemical approaches when the latter are used to investigate the kinetics and mechanisms of reactions occurring in frozen or crystalline states (where, in particular, diffusion-dependent obstacles[123] interfere with the introduction of the required effectors or the substrate by a sufficiently rapid procedure).

We shall indicate two examples. Thus, the flash-induced change in the reactivity of the substrate (or the effector) can be used as a basis for a method whereby the kinetics of the rapid stages of the enzymatic process can be investigated[40,124]; the use of the flash-induced jump in pH merits particular attention in this connection (see Section III, 4).

Another example involves the use of reaction (11) for the investigation of the mechanism of enzymatic catalysis. Fig. 2 shows that the photostereoisomerisation of the substrate residue at the active centre of the acylenzyme proceeds almost instantaneously (there is a rapid increase of the optical density of the solution), but the subsequent chemical stage, namely the hydrolysis of the acylenzyme (a slow increase of the optical density), proceeds with an appreciable induction period. It may be that the observed induction period is due to the conformational-solvation rearrangements in the active centres ensuring the complementarity of the catalyst to the specific substrate produced under the influence of light (as a result of photostereoisomerisation). This explanation is consistent with the hypothesis[125–127] of the conformational (solvation) changes in the active centre, induced by the substrate, which are important for catalysis.

(3) Many of the enzyme systems examined in this review constitute extremely realistic models of more complex light-sensitive systems which function *in vivo*. Analysis of the simple models can therefore assist in a deeper understanding of the principles used by nature to regulate biological activity[14].

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The Influence of the Solvent on the Rates of Chain Propagation and Termination Reactions in Radical Polymerisation

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The influence of the solvent on the rate of radical polymerisation and copolymerisation, observed and investigated in the last ten years and caused mainly by a change in the rate of the elementary chain propagation reaction, is discussed. The published data on the polymerisation and copolymerisation of a number of monomers in solvents of different types are surveyed. Attention is drawn to the fact that the greatest effects are observed for polar monomers, particularly for water-soluble monomers in an aqueous medium. The causes of the change in the overall rate of reaction, the constants k_p, and the copolymerisation constants for different monomers are examined.
The bibliography includes 104 references.

CONTENTS

I.	Introduction	1040
II.	Weakly polar monomers	1040
III.	Polar monomers	1043
IV.	Copolymerisation	1047
V.	Conclusion	1051

I. INTRODUCTION

Various aspects of solvent effects on the kinetics and mechanisms of chemical and particularly chain reactions have been investigated in many studies whose results have been surveyed[1-3]. However, the influence of the solvent on the rate of the chain propagation reaction in polymerisation proceeding via a radical mechanism has been scarcely discussed until recently. It has usually been assumed that the chain propagation and termination rate constants in the initial stages of homogeneous radical polymerisation are independent of the nature of the medium†. The influence of solvents on radical copolymerisation was tested experimentally as early as 1950s. It was established that, in the homogeneous copolymerisation of styrene and methyl methacrylate in benzene and acetonitrile (with dielectric constants of 2.28 and 38.8), the copolymerisation constants are similar. The same result was obtained for the copolymerisation of styrene and 2,5-dichlorostyrene in a number of solvents with markedly different dielectric constants[7]. Significant differences between the reactivities of reacting species as a function of the nature of the medium have been found only in the polymerisation and copolymerisation of certain polar, particularly ionising, monomers[8].

During the last 15–20 years, studies of the influence of the nature of the medium on homogeneous radical polymerisation and copolymerisation have developed extensively in various directions[8-23], including studies on the influence of the solvent on the kinetics and on the structure and properties of polymers. Appreciable effects have been observed in many instances. Furthermore, it has been found that inorganic complex-forming agents (coordination-unsaturated metal compounds) can alter significantly the rates of the elementary reactions and the molecular weights and structures of the polymers. This phenomenon was discovered and investigated in detail by a number of workers[24-27].

Thus the possibility arose of influencing appreciably the rate of chain propagation reactions under the conditions of radical polymerisation. In radical copolymerisation procedures were developed for the regulation and composition and distribution of units in the macromolecule and also of the structure of polymer chains. New ways for the regulation of the properties of the products were devised. Previously no such possibilities were available in radical polymerisation; it was assumed that, in contrast to ionic and ionic-coordination polymerisation, the constants k_p are determined solely by the nature of the monomer—namely by the reactivities of the monomers and the radicals, which are independent of the nature of the medium.

The influences of the solvent on the rates of chain propagation and termination reactions are different, in terms of the magnitude of the effect and frequently its mechanism, for weakly polar and polar monomers.

II. WEAKLY POLAR MONOMERS

Individual observations showing that the influence of solvents on the initial rate of homogeneous radical polymerisation cannot be reduced solely to their involvement in the initiation and chain transfer reactions, were published in several studies as early as the 1950s–1960s.[28-32] It was suggested that polymerisation in solutions involves the formation of complexes between the polymeric radicals and the monomer or solvent molecules. Thus, apart from the interaction with polymeric radicals via a chain transfer

† This review does not deal in detail with the widely known influence of the viscosity of this system on the rate constant for the termination of polymer chains (k_t), which is manifested most significantly at advanced stages of the process. At these stages an increase of the viscosity of the polymerisation system also induces a decrease of the chain propagation rate constant[4] (k_p). The influence of the viscosity of solvents on k_t at the beginning of the reaction has also been demonstrated. Little attention has been devoted to the above problems in the literature (see, for example, Bagdasar'yan[5] and Gladyshev and Popov[6]). The dependence of the rate of initiation on the viscosity of the medium has also been demonstrated[6].

mechanism, in the polymerisation of styrene in bromobenzene the molecules of the latter are probably involved in complex formation[31]. The extremely low rates of polymerisation of vinyl benzoate in bulk could be caused by the formation of a complex of the growing radical with the aromatic ring of the monomer[29]. The appreciable decrease of the rate of polymerisation of vinyl acetate in benzene could also be caused by the formation of a complex between the polymeric radicals and benzene molecules, which leads to the formation of species which are relatively inactive in the chain propagation reaction.

The influence of the nature of the solvent on the overall rate of radical polymerisation of styrene was probably first clearly established experimentally by Henrici Olive and Olive[11-13] A little later the constant k_p and k_t were determined for the polymerisation of methyl methacrylate in a number of solvents[16]. However, the influence of the medium on the rate of radical polymerisation of weakly polar monomers is low: the overall reaction rate changes at the most by a factor of 1.5–2.

The polymerisation of styrene has been investigated in a large number of organic substances of different classes (aromatic and carbonyl compounds, ethers, and alkyl halides) and the dependence of the overall rate of reaction on the nature of the solvent has been demonstrated[11-13]. The observed effect has been examined taking into account the intermolecular interaction between the polymer radicals and the monomer and solvent molecules.

Table 1. The influence of the "τ-ratio" in the polymerisation of styrene in solvents of different classes at 50°C.[13]

Solvent	τ_S/τ_M	Solvent	τ_S/τ_M
Mesitylene	1.62	Tetrahydropyrene	1.01
Methyl isobutyrate	1.53	Anisole	0.97
Dimethoxyethane	1.52	Bromobenzene	0.93
Ethyl acetate	1.44	Dimethylformamide	0.91
Ethylbenzene	1.28	Chloroform	0.90
Toluene	1.28	Pyridine	0.87
Butanone	1.22	Dioxan	0.87
Tetrahydrofuran	1.09	1,2-Dichloroethane	0.85
Benzene	1.04	Methylene chloride	0.83

The electron affinities of typical polymer radicals hardly differ from that characteristic of, for example, tetracyanoethylene and chloranil, which form charge-transfer complexes with the solvents usually employed in vinyl polymerisation. It is therefore assumed that donor–acceptor complexes of polymer radicals with both monomer and solvent molecules arise in polymerisation in solution. The concentration of complex species in the reaction system is proportional to the product of the monomer and solvent concentrations and to the lifetime of the corresponding complexes, which depends on the electronic structure of the species. The influence of the solvent on the rate of polymerisation can be expressed with the aid of a single parameter, namely the "τ-ratio"—the ratio of the lifetime of the donor–acceptor complex between the polymer radical and the solvent molecule (τ_S) to that of the complex between the polymer radical and the monomer molecule (τ_M). The values of the "τ-ratio" for 18 solvents of different classes have been determined from experimental data (Table 1).

The solvent is inert for $\tau_M = \tau_S$. If $\tau_M > \tau_S$, then the rate of polymerisation is higher than in an inert diluent; correspondingly, for $\tau_M < \tau_S$, it is lower. For polymerisation in bulk the "τ-ratio" is unity. Depending on the nature of the solvent, the "τ-ratio" and hence the overall rate of polymerisation of styrene vary at most by a factor of two.

The constants k_p and k_t for the polymerisation of styrene in several solvents have been determined[33] by the usual methods (k_p^2/k_t was obtained from the measured rate of polymerisation and the molecular weights of the polymers, and k_p/k_t was found by the rotating sector method). Table 2 shows that these quantities are somewhat smaller than in the polymerisation of styrene in bulk and decrease with increase of solvent concentration. It has been shown experimentally[33] that k_t is inversely proportional to the viscosity of the solution. The influence of the nature of the solvent on k_p has been explained by the formation of complexes of the growing radicals with the solvent. The stability and reactivity of these complexes determines the difference between the quantity k_p in solution and that of polymerisation in bulk.

Table 2. Photopolymerisation of styrene in solutions at 25°C in the presence of azobisisobutyronitrile[33].

Solvent	$\eta_{mixt.}$, cP	k_p, litre mole^{-1} s^{-1}	$10^{-7}k_t$, litre mole^{-1} s^{-1}
—	11.1	35±7	1.9±0.4
Bromobenzene (50%)	10.5	29±8	1.6±0.3
Bromobenzene (20%)	10.8	35±5	1.9±0.3
Diethyl malonate (20%)	12.1	29±7	1.5±0.4
Diethyl phthalate (50%)	26.1	20±5	0.8±0.2
Diethyl phthalate (20%)	15.2	23±8	1.1±0.2
Dinonyl phthalate (60%)	58.2	27±4	0.31±0.04

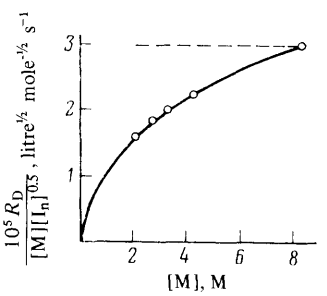


Figure 1. Dependence of the specific rate of polymerisation of styrene $R_p/[M][In]^{0.5}$ on the monomer concentration in the reaction mixture; $[In]/[M] = 0.71 \times 10^{-2}$; dashed line—ideal behaviour.

The influence of the solvent concentration in the reaction system on the overall rate of reaction has also been observed in the polymerisation of styrene in acetone under homogeneous conditions[34]. Here the rate of reaction (R_p) is proportional to the concentration of the initiator (In)

raised to a power of 0.45; however, the dependence of R_p on the monomer concentration differs sharply from linearity (Fig. 1). As in the studies of Henrici-Olive and Olive [11-13], the observed effect is explained by postulating the formation of a complex between the growing polymer radicals and acetone molecules. The formation of complexes between free radicals and various organic compounds has been established experimentally [35]. The stability constants of complexes of the t-butylmesitylnitroxy-radical with various organic substrates (monomers and solvents) as well as their free energies of formation have been determined by gas–liquid chromatography and spectrophotometry. It has been established that solvents forming the most stable complexes exert the greatest influence on k_p in the polymerisation of methyl methacrylate (Fig. 2). The formation of complexes between a stable radical (2,2,6,6-tetramethylpiperidinyl-1-oxy-radical) and methacrylate esters has also been established [36] by NMR and EPR.

The hypothesis put forward by Henrici-Olive and Olive [11-13] was confirmed in a study [16] of the photopolymerisation of methyl methacrylate in fluoro-, chloro-, and bromo-benzenes, anisole, and benzonitrile. The rate of polymerisation is somewhat higher in all these solvents than in benzene. Although all the values of k_p lie within the limits of the accuracy of the determination, nevertheless according to the authors [16] they increase steadily in the sequence benzene < fluorobenzene < chlorobenzene < anisole < bromobenzene < benzonitrile. The values of k_t vary in inverse proportion to the viscosity of the solvent.

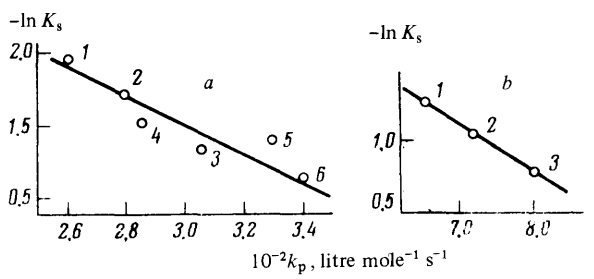


Figure 2. Dependence of k_p for the polymerisation of methyl methacrylate in different solvents at 25° (*a*) and 60°C (*b*) on the stability constants of the complexes of the t-butylmesitylnitroxy-radical with the solvents: *a*) [1) benzene; 2) chlorobenzene; 3) bromobenzene; 4) anisole; 5) benzonitrile; 6) methyl benzoate]; *b*) [1) 1-fluoronaphthalene; 2) 1-chloronaphthalene; 3) 1-bromonaphthalene].

The polymerisation of methyl methacrylate in solutions in halogeno-derivatives of benzene and naphthalene has been investigated in a series of studies [37-40]. The rate of polymerisation in monosubstituted aromatic hydrocarbons is higher than that in benzene and varies with the nature of the halogen in the sequence fluorobenzene < chlorobenzene < bromobenzene < iodobenzene, i.e. increases with decrease of the electronegativity of the substituent. Under identical conditions, the overall rate of reaction is 0.19 wt. % min^{-1} in benzene and 0.35 wt.% min^{-1} in iodobenzene. Dihalogenobenzenes increase the overall rate of polymerisation of methyl methacrylate to a somewhat greater extent than the monosubstituted derivatives and the 1,2-isomer is more effective than the 1,3- or 3,4-isomers. The nature of the substituent has the same influence in this case as for monosubstituted benzene derivatives. Di- and tetrabromobenzenes do not affect the rate of polymerisation.

It has been suggested [37-39] that the main cause of the influence of the solvent is a change in the rate of initiation. However, determination of the absolute rate constants for the elementary chain propagation and termination reactions as well as the rates of initiation in the polymerisation of methyl methacrylate in solution and halogenonaphthalenes [40] showed that the rate of initiation remains almost constant and the effect is due to a slight change in k_p and k_t. The constant k_t varies inversely with the viscosity of the solution; on the other hand, the variation of k_p is probably due to the formation of a complex with the solvent. As in the study of Bamford and Brumby [16], it was found that [37-40] the overall effect of the solvent on k_p is extremely small. On the basis of the results obtained in the polymerisation of methyl methacrylate in halogenated aromatic solvents in the presence of an inhibitor, it has been concluded [41] that the solvent affects mainly the constant k_t.

A slight increase of the overall rate of polymerisation, due to the increase of the ratio $k_p/k_t^{1/2}$, is also observed in the polymerisation of methyl methacrylate in aromatic solvents [42]. The rate of reaction increases in the sequence toluene < *p*-chlorotoluene < benzene < bromobenzene.

In the polymerisation of methyl methacrylate in ethereal solvents [43] a change in the overall rate of reaction as a function of the nature of the solvent is also observed. Here too, the change in k_t, associated with the different viscosities of the solution, exerts the main influence; however, the change in k_p, reaching 20–25%, also has some effect. Analogous results were obtained in the study of the polymerisation of benzyl methacrylate in ethereal solvents differing in viscosity [44] and also in the polymerisation of tetrahydrofurfuryl methacrylate [45] and phenyl methacrylate [46] in various media. The constant k_p for benzyl methacrylate increases somewhat with increasing viscosity of the solution (by 30–35%).

Table 3. Polymerisation of vinyl benzoate in different solvents at 30°C. [46]

Solvent	k_p, litre mole^{-1} s^{-1}	$10^{-8}k_t$, litre mole^{-1} s^{-1}
Anisole	106	2.53
Benzene	185	4.02
Fluorobenzene	245	5 22
Chlorobenzene	168	3.83
Ethyl benzoate	69	2.57
Benzonitrile	33	2.99
Ethyl acetate	267	4.51

Much greater effects are observed in the polymerisation of vinyl benzoate [46] in various aromatic solvents (Table 3). The change in the constant k_p in this system is probably due to the formation of π-complexes between solvent molecules and the growing radical, which leads to a significant alteration in the reactivity of the radicals. The constants k_t are inversely proportional to the viscosity of the reaction system.

The overall rate of homogeneous polymerisation of cyclohexyl and cyclododecyl acrylates increases in the following sequence of solvents: benzene < tetrahydrofuran < dioxan[47]. Thus at 60°C (azobisisobutyronitrile concentration 0.01 M, monomer concentration 0.8 M), the overall rates of polymerisation ($10^5 R_p$, mole litre^{-1} s^{-1}) of cyclododecyl acrylate are 15.1 in benzene, 21.3 in tetrahydrofuran, and 60.0 in dioxan. Under analogous conditions, the overall rates of polymerisation of cyclohexyl acrylate are 9.87, 11.6, and 22.1 respectively. The change in the overall rate of the process is caused, according to the authors[47], by the different degrees of polarisation of the carbonyl group in the acrylate monomer in the solvents investigated. It had been found earlier[48] that the polarisation of the carbonyl group ($\rangle C^+=O^-$) of methyl methacrylate increases the reactivity of this monomer in its copolymerisation with styrene. It has been established by infrared spectroscopy[47] that (the carbonyl groups of) cyclohexyl and cyclododecyl acrylates are polarised to a greater extent in solutions in dioxan and tetrahydrofuran than in benzene solutions. The change in the overall rate of polymerisation is therefore probably associated in this case with the change in k_p.

The influence of the solvent on the rate of polymerisation has also been demonstrated for the homogeneous polymerisation of vinyl chloride[49]. The ratio $k_p/k_t^{1/2}$ for the polymerisation is 0.68 in dichloroethane (50°C) and 0.19 in benzene.

III. POLAR MONOMERS

The influence of the nature of the medium has been found to be much greater in the polymerisation of vinyl polymers containing heteroatoms with a lone electron pair and capable of involvement in the formation of hydrogen bonds‡.

At the beginning of the 1960s it was already shown[50-53] that the rate of polymerisation of a number of monomers in bulk is related to the presence or absence of intermolecular hydrogen bonds in these substances. Thus the rates of polymerisation of the *o*-isomers of ethoxy- and methoxy-phenylmethacrylamides, ethoxy-phenylacrylamide, chlorophenylmethacrylamide, biphenylylmethacrylamide, and carboxyphenylmethacrylamide exceed the rates of polymerisation of the *m*- and particularly *p*-isomers. This is because the *o*-isomers of these compounds exist in the form of unassociated molecules, while the *m*- and *p*-isomers form associated species via hydrogen bonding. The presence of associated structures in the *m*- and *p*-compounds has been established[50-53] by infrared spectroscopy. One should note that in the case of tolylmethacrylamide, where all the isomers are capable of forming associated species via hydrogen bonding, the rates of polymerisation of the isomers do not differ from one another[51].

Presumably the addition of certain solvents, capable of dissociating intermolecular hydrogen bonds and thus preventing the association of monomer molecules, to the monomer present in the associated form leads to an alteration of the rate of its polymerisation.

A very appreciable influence of the solvent on the overall rate of polymerisation and the chain propagation rate constant has been established for acrylamide and methacrylamide[21,54]. The polymerisation was studied in water, dimethyl sulphoxide (DMSO), and tetrahydrofuran (THF) under the influence of azobisisobutyronitrile. In water and DMSO acrylamide polymerises under homogeneous conditions, while the polymerisation of acrylamide in THF and also that of methacrylamide in all the solvents investigated takes place heterogeneously. However, in all cases the reaction in dilute solutions takes place at the beginning of the process at a constant rate which is proportional to the monomer concentration and the square root of the initiator concentration. The overall rate of polymerisation of acrylamide and methacrylamide decreases significantly in the sequence water > DMSO > THF. The average molecular weights of the acrylamide polymers decrease in the same sequence. The ratio $k_p/k_t^{1/2}$ measured for acrylamide decreases to an even greater extent, since the rate of initiation varies in the opposite sequence. Thus at 40°C the ratio $k_p/k_t^{1/2}$ is 3.3 in water, 0.35 in DMSO, and only 0.05 in THF.

An appreciable increase of the overall rate of reaction and of the molecular weight of the polymer with increasing water content in the solvent has been observed in the polymerisation of acrylamide in water–methanol mixtures[55,56]. A similar influence of water has been observed also for the polymerisation of acrylamide in water–DMSO mixtures[57].

Table 4. Polymerisation of acrylamide in various solvents[22,54].

Solvent	$k_p/k_t^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{-1/2}$ (40°C)	E_p, kcal mole^{-1}	$10^{-7}A_p$, litre mole^{-1} s^{-1}	E_t, kcal mole^{-1}	$10^{-8}A_t$, litre mole^{-1} s^{-1}
Water (pH 7)	4.1	2.7	1.0	2.7	780
Water (pH 13)	3.6	3.6	2.2	1.0	9.7
Formamide	1.0	5.0	4.4	0.8	7.2
DMSO	0.32	5.4	3.0	0	2.5
Tetrahydrofuran	0.05				

The photopolymerisation of acrylamide (sensitised by azobisisobutyronitrile) has been studied in greater detail in water at pH 7 and 13, formamide, and DMSO[21,22,58]. The constants k_p and k_t and the corresponding activation energies were determined separately (Table 4). It was established that, compared with k_p for the polymerisation in water at pH 7, the constant k_p at 20°C is smaller by a factor of 2 in water at pH 13, by a factor of 12 in formamide, and by a factor of 35 in DMSO. The decrease of k_p is caused by the increased activation energy for this reaction: the pre-exponential factors are almost the same or change only slightly in the opposite sequence. The values of k_t, activation energies, and pre-exponential factors for this reaction (A_0) are the same in all the solvents investigated with the exception of water at pH 7. In the latter case higher values were obtained for E_0 and A_0. The

‡ The results of certain studies concerning the influence of the solvent on the radical polymerisation of polar monomers (acrylic acids, vinylpyridines, and *N*-vinylpyrrolidinone) and also on their copolymerisation with other vinyl monomers have been described in a recently published monograph[8] and are therefore not considered in detail in the present review.

latter quantity is higher than for other solvents by two orders of magnitude, so that ultimately k_t is somewhat higher despite the greater activation energy (2.7 kcal mole^{-1} compared with 0–1 kcal mole^{-1}).

The observed influence of the solvent on the kinetic parameters of the polymerisation process can probably be explained by the intermolecular interaction of the acrylamide molecules with one another (in the monomeric and polymeric forms) and also with solvent molecules. The different extents of this interaction are indicated by the heats of solution and polymerisation of acrylamide in certain solvents [22,59] (Table 5) and also by the results of cryoscopic measurements, which showed that the degree of association of acrylamide molecules is 1.30 in DMSO and 1.15 in formamide; in aqueous solution (at pH 7 and 13) acrylamide is almost non-associated. The heat of polymerisation of acrylamide also depends on the nature of the solvent. The polymerisation in aqueous solution has the highest heat, the latter being significantly smaller in organic media. The dependence of the heat of polarisation on the nature of the solvent shows that monomer molecules are associated to a greater extent than the polymer radicals and polymer molecules [59].

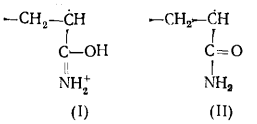
Table 5. Heats of solution and polymerisation of acrylamide and methacrylamide in various solvents [22,59].

Solvent	ΔH, kcal mole^{-1}			Solvent	ΔH, kcal mole^{-1}		
	of soln.	of polymerisation	of polymerisation		of soln.	of polymerisation	of polymerisation
	acrylamide		methacrylamide		acrylamide		methacrylamide
Water (pH 7)	−2.9	19.5	13.4	Chloroform	—	—	10.2
Water (pH 13)	−2.75	—	—	Acetone	—	16.9	9.4
Formaide	−2.5	—	—	Benzene	—	14.4	8.4
DMSO	−1.1	—	—	n-Hexane	—	13.8	—

Such intermolecular interaction makes the energy levels of the initial and final states in the polymer chain propagation reaction dependent on the nature of the solvent. For polymerisation in aqueous solutions the activation energy for the chain propagation reaction is therefore lowest and the heat of reaction highest. In formamide and DMSO, where the monomer molecules interact via hydrogen bonds, the activation energy for the propagation reaction is significantly higher, since it includes the energy necessary for the dissociation of the intermolecular hydrogen bonds.

Since the heat of polymerisation of methacrylamide in various solvents changes in the same way as for acrylamide [59], the decrease in the rate of polymerisation of this monomer in the sequence water > DMSO > THF is apparently due to the same causes.

The most intense solvation of acrylamide by solvent molecules is observed in aqueous solution. In the limiting case there is a possibility of a chemical reaction between acrylamide and the protons formed in the dissociation of water, because acrylamide has weakly basic properties. This reaction takes place with acrylamide radical to a greater extent, because the presence of an unpaired electron probably leads to an increase of the basicity of the radical compared with the neutral molecule, increasing thereby the equilibrium constant of the protonation reaction. The addition of a proton to the oxygen atom [60] of the acrylamide radical (I) and the consequent appearance of a positive charge at the nitrogen atom lead to the localisation of the unpaired electron and to an increase in the reactivity of the radical:



(I) (II)

In the non-protonated radical (II) there is a possibility of the conjugation of the unpaired electron with the C=O double bond; in radical (I) there is no such conjugation. The positive charge of the nitrogen atom draws the π electrons of the C=N double bond towards itself, which prevents the conjugation of the unpaired electron with this double bond.

The idea of the higher reactivity of the acrylamide radical in water as a result of the addition of a proton and of the involvement of this radical to some extent in the chain propagation and termination reactions is confirmed by the following experimental data: (1) the increase of the chain propagation and termination rate constants in the polymerisation of acrylamide in aqueous solution with decrease of the pH of the medium from 13 to 1 (Currie et al. [61]); (2) the increase of k_t for the reactions in water at pH 7 compared with the value of k_t for the polymerisation in water at pH 13, formamide, and DMSO. The activation energy for the termination of polymer chains in water at pH 7 is 1.7–2.7 kcal mole^{-1} higher than in other solvents. The difference is probably due to the energy expended on overcoming the repulsion of the charged polymer radicals.

The higher rates of chain propagation in the polymerisation of acrylamide in aqueous solution compared with the polymerisation in formamide and DMSO are caused both by more favourable solvation conditions in water and by a definite role of the hydrogen ion formed by the dissociation of water in interacting with the amide group of the growing chain. The two factors are interrelated and undoubtedly exert a parallel influence on the rate of polymerisation of acrylamide. The role of the second factor naturally increases with increase of the concentration of H^+.

The formation of insoluble polyacrylamide in neutral and particularly in acid concentrated aqueous solutions is associated with the presence of hydrogen ions and probably protonated acrylamide radicals (I). [62] This hypothesis is supported by the following facts: (1) polymerisation in alkaline concentrated aqueous solutions yields a fully soluble polymer; (2) the polymerisation of acrylamide in neutral and acid concentrated aqueous solutions in the presence of β,β',β'', nitrilotripropionamide, which is a stronger proton acceptor than acrylamide, is not accompanied by the cross-linking of the polymer chains; (3) in concentrated solutions in an aprotic solvent (DMSO) soluble polymers are formed at advanced stages of the reaction.

A fairly large number of studies [63–67] have been devoted to the investigation of the influence of the nature of the solvent on the polymerisation of acrylic and methacrylic acids§. Acrylic acid polymerises in bulk under the influence of γ-radiation at a very high rate with formation of

§The polymerisation of ionogenic monomers, particularly acrylic and methacrylic acids at different pH values as well as dioxan in the presence of complex-forming agents, has been examined in detail in a monograph [8].

high-molecular weight stereoregular polymers (with a molecular weight up to 3×10^7). The activation energy for this process in the temperature range from 20° to 70°C is only 2.7 kcal mole^{-1}. Solvents capable of forming hydrogen bonds with the monomer (water, methanol, acetic acid, and dioxan) do not alter significantly the rate of polymerisation of acrylic acid when they are added in an amount of 20–25%. None of these solvents (with the exception of water) influences the syndiotacticity of polyacrylic acid. On the other hand, small amounts of chloroform (5–10%) and hydrocarbon solvents (n-hexane and toluene) reduce appreciably the overall rate of polymerisation and the syndiotacticity of the polymer.

In order to account for these results, it has been suggested[63-67] that, apart from dimeric cyclic aggregates (characteristic of carboxylic acids), acrylic acid gives rise to a linear high-molecular weight aggregate structure, where the distribution of vinyl groups favours a very rapid chain propagation and the formation of a syndiotactic polymer. The addition of water, methanol, and dioxan leads to the binding of the linear acrylic acid aggregates to one another. In contrast to this, benzene, toluene, n-hexane, and chloroform disrupt the linear aggregates. Such changes in the structure of the aggregates of polymeric molecules in the solvents investigated are in fact responsible for the different kinetic characteristics of the polymerisation of acrylic acid in these solvents. The observed[65] sharp increase in the rate of polymerisation of acrylic acid in n-hexane when the temperature is raised from 20° to 40°C has also been explained by the equilibrium transition from cyclic dimers to linear associated species as the temperature is increased.

However, there is apparently no need to resort to ideas about the formation of high-molecular weight aggregates in acrylic acid solutions in order to account for the results obtained[63-67], particularly since according to some data[23,68], obtained by the cryoscopic method, acrylic acid exists in the form of individual molecules in water and formamide, while in solution in DMSO it is associated only to the extent of approximately 10%. It has been shown[69] that the reactivity of the dimerised acrylic acid is lower than that of the non-dimerised acid. The difference between rates of polymerisation of this monomer, observed in different solvents, can therefore be caused by the fact that acrylic acid in bulk exists in the form of dimers, which dissociate to some extent into individual molecules as a result of the formation of hydrogen bonds with solvent molecules in solutions in water and other polar solvents but are little altered in hydrocarbon media. In non-polar solvents, particularly in n-hexane, an increase of temperature favours the dissociation of the acid dimers, which leads to a marked temperature dependence of the rate of polymerisation in n-hexane.

In examining the results of the above studies[63-67], one must therefore take into account the phase state of the reaction system, which depends on the nature and amount of the solvent. Indeed, whereas in the polymerisation of acrylic acid in dilute solutions in water, methanol, and dioxan, the reaction proceeds in a homogeneous system, when acetic acid, toluene, n-hexane, and chloroform are used as solvents and also in polymerisation in bulk the resulting polymer is produced in the form of a new phase, which greatly complicates the kinetic picture of the process.

The influence of the nature of the solvent on the polymerisation of acrylic acid and its derivatives, (methacrylic and α-fluoroacrylic acids) has been investigated in greater detail in other investigations[23,68,70-72]. The homogeneous polymerisation has been studied in water, formamide, and DMSO. The overall rate of polymerisation is a maximum in water and diminishes on passing to formamide and then to DMSO. The reaction proceeds in all cases at a rate proportional to the concentration of the monomer and to the square root of the concentration of the initiator. The data in Table 6 show that the increase of the overall rate of the process is accompanied by the increase of k_p owing to the decrease of the activation energy for this reaction. At the same time the results indicate a significant difference in the behaviour of acrylic acid and its α-derivatives. Whereas in the polymerisation of acrylic acid a sharp dependence of the overall rate of reaction and of k_p on the nature of the solvent is observed, for methacrylic and particularly fluoroacrylic acids, the influence of the medium is much less. Thus k_p decreases by a factor of 50 on passing from water to DMSO for acrylic acid, by a factor of 25 for methacrylic acid, and only by a factor of 3 for fluoroacrylic acid.

Table 6. Parameters characterising the chain propagation and termination reactions in the polymerisation of acrylic (AA), fluoroacrylic (FAA), and methacrylic (MAA) acids in various solvents[71,72].

Monomer	k_p, litre mole^{-1} s^{-1} (20°C)	E_p, kcal mole^{-1}	$10^{-7}A_p$, litre mole^{-1} s^{-1}	$10^{-8}k_t$, litre mole^{-1} s^{-1} (20°C)	E_t, kcal mole^{-1}	$10^{-8}A_t$, litre mole^{-1} s^{-1}
			Water			
AA	27 200	3.1	0.60	1.8	0	1.8
MAA	4 100	4.3	0.67	0.12	0.2	0.16
FAA	2 600	4.5	0.60	0.87	0.6	2.0
			Formamide			
AA	4200	5.6	6.2	1.0	0	1.0
FAA	2200	4.9	0.75	0.74	0.4	1.5
			DMSO			
AA	500	8.0	47	0.2	0	0.2
MAA	150	7.3	4.1	0.09	1.0	0.48
FAA	850	5.2	0.66	0.49	0.4	1.0

It follows from cryoscopic data[68] that the observed influence of the solvent on the rate of the chain propagation reactions involving acrylic acids cannot be associated solely with the different degrees of association of the monomeric molecules in the solvents, as has been suggested for acrylamide[22]. Indeed, although acrylic acid is in fact partly dimerised in solution in DMSO, the concentration of dimers does not exceed 10%, so that their contribution cannot probably be decisive. Acrylic acid in aqueous solution and fluoroacrylic acid in solutions in water and in DMSO are present in the form of individual molecules.

As for acrylamide, the heats of solution and polymerisation of acrylic and fluoroacrylic acids vary with the nature of the medium (Table 7). However, the heats of solution of acrylic and fluoroacrylic acids in DMSO and formamide change in the same way for both monomers: the dissolution in water is accompanied by the absorption of heat; on passing to formamide and DMSO, the heat of solution increases. However, the heats of polymerisation of these monomers vary in different ways as a function of the nature of the solvent. Whereas the heat of polymerisation of acrylic acid in water is significantly greater than in DMSO

(18.5 and 14.1 kcal mole^{-1} respectively), the heat of polymerisation of fluoroacrylic acid in these solvents is virtually the same (~ 13 kcal mole^{-1}).

Table 7. Heats of solution and polymerisation of acrylic (AA) and fluoroacrylic (FAA) acids in various solvents[72].

Monomer	ΔH, kcal mole^{-1}		Monomer	ΔH, kcal mole^{-1}		Monomer	ΔH, kcal mole^{-1}	
	of soln.	of polymerisation		of soln.	of polymerisation		of soln.	of polymerisation
	Water			Formamide			DMSO	
AA	−0.2	18.5	AA	0.6	—	AA	3.0	14.1
FAA	−2.3	13.3	FAA	−1.1	—	FAA	0.3	13.0

The observed difference between the heats of polymerisation of acrylic acid in the solvents investigated can be due to the different conformational states of the polymer molecules in these media. Water is a better solvent for polyacrylic acid than DMSO. The polymer chain therefore exists in water in the form of looser coils than in DMSO, which promotes a more effective penetration of the solvent into the polymer coil in aqueous solution. This difference between the states of the polymer molecules in water and in DMSO leads to an appreciably higher energy of solvation of polyacrylic acid molecules in aqueous solution compared with the solution in DMSO which is the reason for the difference between the heats of polymerisation [because the solvation energies (heats of solvation) of the monomer and its saturated analogue are virtually the same[73,74]].

The greater density of the polymer coil of polyacrylic acid in DMSO compared with aqueous solutions leads to a lower rate of bimolecular polymer chain termination in DMSO compared with water (Table 6). The introduction of a fluorine atom into the polymer chain increases the rigidity of the chains, as a result of which the influence of the solvent on the conformational state of the macromolecules and hence also on the heat of polymerisation is much smaller for fluoroacrylic acid than for acrylic acid.

As for acrylamide[22], the decrease of the activation energy for chain propagation in the polymerisation of acrylic and fluoroacrylic acids is accompanied by an increase in the heat of polymerisation, i.e. the Polanyi–Semenov rule holds qualitatively. For isotypical reactions the following equality is valid[75]: $\Delta E = -\alpha\Delta(\Delta H)$, where $\alpha \simeq 0.25$ for the usual radical reactions. It follows from a comparison of the values of ΔH and E_p for the polymerisation of acrylic and fluoroacrylic acids in water that $\alpha = 0.26$. However, α for the polymerisation of acrylic and fluoroacrylic acids in DMSO exceeds 1.0. The value $\alpha > 1.0$ is also obtained on comparing the results for acrylic acid in water and in DMSO.

The failure of the Polanyi–Semenov rule can indicate a different nature of the reacting species in the solvents investigated. This is also suggested by data for the compensation effect observed in the polymerisation of acrylic acid in different solvents (see Table 6). The presence of the compensation effect in liquid-phase radical reactions can be due[2] to the specific interaction of the radicals with the medium (particularly the formation of π-complexes).

It has been suggested[11–13] that free radicals are capable of forming π-complexes with solvents exhibiting electron-donating properties. The formation of complexes of this kind has been shown[76] to lead to decreased unpaired electron density in the radical, which decreases the reactivity of the latter. The solvents employed[68,70–72] are electron donors under the conditions investigated, the electron-donating capacity increasing in the sequence water < formamide < DMSO. The complex between the polymer radical and the solvent is therefore most probably formed in solution in DMSO, which leads to the maximum reactivity of the polymer radical in this solvent. The probability of the radical forming of a complex with formamide and particularly with water is lower; consequently, the reactivity of the radical in these media diminishes to a smaller extent than in DMSO; this leads to the experimentally observed dependence of k_p on the nature of the solvent.

The formation of complexes between solvent molecules and polymer radicals should be reflected also in the energetics of the chain propagation reaction. In the transition state a complex between the radical and the solvent probably has to be decomposed in order to achieve the chain propagation reaction; this requires an additional energy, which is part of the activation energy for the chain propagation process. Since the formation of a radical–solvent complex takes place to the greatest extent in DMSO, the energy E_p for polymerisation should also be a maximum in this case.

The probability of the formation of complexes between the solvent and the polymer radical apparently decreases with decreased reactivity of the radical. In the polymerisation of methacrylic and especially fluoroacrylic acids, whose polymer radicals are less reactive than the radicals of polyacrylic acids, the influence of the nature of the medium is therefore less pronounced than for acrylic acid.

Thus the different effects of the nature of the solvent on the polymerisation of acrylic, methacrylic, and fluoroacrylic acids reduce the reactivity of the initially more reactive radical, formed from acrylic acid (the reactivity of this radical is characterised by the constant k_p in water, where the probability of the formation of a complex with the solvent is low), compared with the fluoroacrylic and methacrylic acid radicals in DMSO—a solvent capable of forming a complex with this radical.

Table 8. Polymerisation of methacrylic acid in various solvents at 10°C.[77]

Solvent	k_p, litre mole^{-1} s^{-1}	$10^{-7}k_t$, litre mole^{-1} s^{-1}
Methanol	517	3.7
Pyridine	527	2.3
Dimethylformamide	28	0.44

The polymerisation of methacrylic acid in different solvents has also been investigated by Shryver et al.[57] The reaction was carried out under the influence of azobisisobutyronitrile at 60°C. The authors showed that the addition of water to organic solvents (ethanol, ethanol–dioxan, and DMSO) increases significantly the overall rate of polymerisation and the molecular weight of the polymers. One should note particularly that the rate of reaction is almost independent of the dielectric constant of the reaction mixture and is determined by its water content. In this case the observed effect can probably be accounted for by the different degrees of complex formation between the polymer radicals and solvent molecules.

The polymerisation of methacrylic acid in methanol and pyridine is characterised by identical constant k_p and k_t (Table 8); in the polymerisation in dimethylformamide the above constants are significantly lower[77]. The observed change in the rate constants for the chain propagation and termination reactions has been attributed[77] to the polar effect, which changes as a function of the solvent. However, in this case the different degrees of association of the acid molecules in the solvents is also presumed to have a significant influence. Owing to the formation of hydrogen bonds between the acid and solvent molecules, in methanol and pyridine the degree of dimerisation of methacrylic acid is appreciably lower than in dimethylformamide, which is indicated by spectroscopic data[77]. The reactivity of dimerised methacrylic acid is lower, as with acrylic acid[68], than that of the non-dimerised acid.

A change in the degree of ionisation of the acid can also exert a definite influence on the polymerisation of acrylic acids in solvents of different polarity. Kabanov and coworkers[8] showed quite definitely that the reactivity of the ionised acid is much lower than that of the unionised acid.

Taking into account the different degrees of dimerisation and ionisation, it is possible to explain the results obtained in the polymerisation of butadiene-1-carboxylic acid in different electron-donating solvents[78]. The rate of polymerisation of this monomer under the influence of azobisisobutyronitrile increases in the sequence dimethylformamide < tetrahydrofuran < ethyl methyl ketone < acetonitrile < benzene.

Among the polar monomers for which the rate constants for the elementary chain propagation and termination reactions have been determined in different solvents, mention should be made also of *N*-vinylpyrrolidinone. It has been shown in an early study[79] that the rate of its radiation-induced polymerisation depends significantly on the nature of the solvent. The overall rate of reaction increases appreciably on passing from methanol to ethanol, isopropyl alcohol, and t-butyl alcohol. An even greater increase in the rate of the radiation-induced polymerisation was observed after the addition of water to methanol. Thus, following the addition of 25, 50, and 75% of water, the overall rate of reaction increased from 0.5–0.8 wt.% min^{-1} to 1.7, 3.5, and 5.75 wt.% min^{-1} respectively. Whereas the increase of the reaction rate in different alcohols can be accounted for by the increased rate of initiation owing to the change in the radiation-chemical yield of the initiation process (G_{in}), for aqueous methanol solutions the change in G_{in}, even if it is observed, cannot explain the sharp change in the overall rate of polymerisation.

Table 9. Polymerisation of *N*-vinylpyrrolidinone in various solvents at 26°C.[70]

Solvent	$k_p/k_t^{1/2}$, litre$^{1/2}$ mole$^{-1/2}$ s$^{-1/2}$	k_p, litre mole^{-1} s^{-1}
Tetrahydrofuran	0.08	400
Dichloroethane	0.08	400
Methanol	0.17	870
N-Vinylpyrrolidinone	0.15	1200
Water	1.40	>3500

In the study of the homogeneous polymerisation of *N*-vinylpyrrolidinone in different solvents it was established that the reaction under the influence of azobisisobutyronitrile can proceed in solution in methanol at a higher rate than in tetrahydrofuran or dichloroethane[80]. It follows from Table 9 that an increase of the overall rate of the process in methanol is almost fully due to the higher constant k_p. The change in k_p is in its turn related to the change in E_p: for virtually identical pre-exponential factors A_p (3.16×10^8 and 3.4×10^8 litre $mole^{-1}$ s^{-1} in methanol and tetrahydrofuran respectively), E_p for the polymerisation in methanol is smaller by 0.5 kcal $mole^{-1}$ than in tetrahydrofuran (7.6 and 8.1 kcal $mole^{-1}$ respectively).

The homogeneous polymerisation of *N*-vinylpyrrolidinone in bulk[81] and particularly in aqueous solution[70] is characterised by an even greater increase of the overall rate of the process (of the ratio $k_p/k_t^{1/2}$) than in methanol, compared with polymerisation in tetrahydrofuran and dichloroethane (Table 9). Here too, the change in the overall rate of polymerisation is accompanied by a change in k_p. In terms of their influence on k_p in the polymerisation of *N*-vinylpyrrolidinone the solvents can be arranged in the following sequence: tetrahydrofuran, dichloroethane < methanol < *N*-vinylpyrrolidinone < water. Evidently the increase in solvent polarity leads to an increase of k_p, which can be attributed to the influence of the solvent on the distribution of electron density in the pyrrolidinone ring and hence on the reactivity of the monomer and the radical formed from it. Neither can one rule out the influence of complex formation between the polymer radicals and the solvent, which varies as a function of the nature of the solvent.

IV. COPOLYMERISATION

The different reactivities of the monomers in different solvents can lead to the variation of the rate of copolymerisation and the composition of the copolymers. The results of studies on the influence of the medium on copolymerisation involving acrylic and methacrylic acids as well as their amides are examined below, because the influence of the nature of the solvent on the reactivities of these monomers is most significant.

Many studies have been devoted to the copolymerisation of methacrylic and acrylic acids with certain vinyl monomers in solvents of different types. Both acrylic and methacrylic acids are known to exist in bulk phase as dimers, whose reactivity differs from that of the non-dimerised monomer molecules[69]. However, in many solvents the dimers decompose owing to the specific interactions between the acid and solvent molecules. In addition, one should bear in mind that the degree of ionisation of acid molecules can change with the polarity of the solvent, which should also be reflected in the reactivity of the acids. The composition of the copolymers of these acids with other monomers therefore usually depends on the nature of the solvent.

In the copolymerisation of methacrylic acid with methyl methacrylate or styrene the addition of dimethyl formamide or ethanol to the mixture of monomers reduces the content of the acid units in the copolymer[82] and dimethylformamide influences the composition of the copolymer to a much greater extent than does ethanol (Fig. 3). The decreased reactivity of methacrylic acid is caused by the formation of a complex with the solvent via –H...O–C hydrogen bonds, which is indicated by the appearance of a sharp maximum on the curve describing the variation of the viscosity of solutions of the acid in dimethylformamide or ethanol, as well as spectroscopic data. For mixtures of methyl methacrylate with dimethyl formamide, a linear

relation between the viscosity and mixture composition has been observed. The addition of water to the methyl methacrylate–methacrylic acid system also reduces the number of acid units in the copolymer[83].

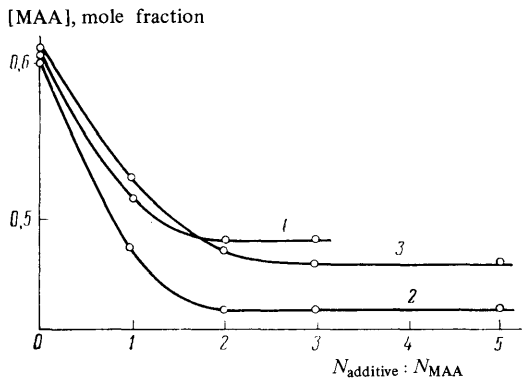
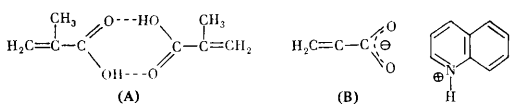


Figure 3. Variation of the content of methacrylic acid (MAA) in the copolymers formed in equimolar mixtures of methyl methacrylate (curves *1* and *2*) with methacrylic acid as the content of ethanol (curve *1*) and dimethylformamide (curve *2*) is increased and also in equimolar mixtures of styrene (curve *3*) with MAA as the content of dimethylformamide in the reaction mixture is increased.

The addition of Lewis bases (tetrahydrofuran, quinoline, pyridine, and DMSO) to the methacrylic acid–styrene system reduces the reactivity of methacrylic acid[84], pyridine and DMSO having the greatest effect. The reactivity of methacrylic acid decreases in their presence and the resulting copolymers are depleted in methacrylic acid compared with the copolymers synthesised in the absence of a solvent. It has been suggested[84] that in the presence of electron-donating solvents, for example quinoline, methacrylic acid can exist in two forms:



The reactivity of methacrylic acid in copolymerisation depends on the quantitative ratio between forms (A) and (B), which is determined in its turn by the nature of the solvent. The greater the amount of acid in form (B), the electropositive properties of the double bond of which are less marked than in (A), the lower the reactivity of the monomer in copolymerisation with styrene.

An appreciable variation of the constants for the copolymerisation of acrylic acid with styrene and methyl methacrylate as a function of the nature of the solvent has been observed[69,85,86]. Whereas for the reaction in bulk the constants for the copolymerisation of styrene with acrylic acid at 50°C are 0.25 (styrene) and 0.15 (acrylic acid), in solvents capable of forming hydrogen bonds with acrylic acid the relative reactivity of this monomer diminishes. In ethyl methyl ketone, dioxan, tetrahydrofuran, and dimethylformamide the copolymerisation constant is virtually invariant for the acid (0.13–0.15), but that for styrene changes from 0.70 (in ethyl methyl ketone) to 1.03 (in dimethylformamide), which indicates a decrease of the reactivity of acrylic acid. Analogous results were obtained for the copolymerisation of acrylic acid with methyl methacrylate[85,86]. A correlation has been established between the copolymerisation constants (for styrene and methyl methacrylate) and the stability constants of the complexes between acrylic acid and the solvent. One should note that the observed changes in the copolymerisation constants in the solvents investigated are not related to the different reactivities of the dissociated and undissociated acrylic acid, since a correspondence between the copolymerisation constants and the dielectric constants of the solvents has not been observed.

A more complete survey on studies of the influence of the medium on the copolymerisation of methacrylic and acrylic acids as well as vinylpyridines with other monomers, published up to 1973, has been carried out by Kabanov and Topchiev[8].

The different reactivities of the radicals formed from acrylic and fluoroacrylic acids in different solvents, established in a number of investigations[23,68,70-72], lead to a significant dependence of the rate of copolymerisation and the composition of the copolymers of these acids on the nature of the reaction medium[87]. Whereas in aqueous solution the addition of even small amounts of fluoroacrylic acid to acrylic acid entails a sharp decrease in the rate of the process, a different behaviour is observed in solution in DMSO (Fig. 4), where the rate of reaction passes through a small maximum as a function of the composition of the initial monomer mixture at low fluoroacrylic acid concentrations (20 mole%) and then gradually diminishes, reaching values characteristic of the rates of the separate polymerisation of acrylic and fluoroacrylic acids.

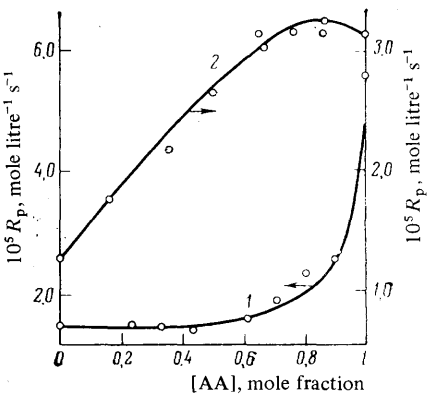


Figure 4. Dependence of the rate of copolymerisation of acrylic and α-fluoroacrylic acids on the composition of the mixture of monomers in copolymerisation in water (1) (initiator concentration 5×10^{-4} M) and in DMSO (2) (initiator concentration 4×10^{-3} M); $[M_1] + [M_2] = 1$ M.

The copolymerisation constants for the given pair of monomers are r_1(AC) = 0.5 and r_2 = 1.5 for copolymerisation in water, and r_1 = 0.5 and r_2 = 0.7 in DMSO. The rate constants for the addition of the radical to a "foreign" monomer (Table 10) have been calculated from the copolymerisation constants and rates of separate chain propagation[68]

(Table 10). These results show that, in the copolymerisation in water, the reactivities of the monomers and radicals differ strongly: the more reactive radical is that of acrylic acid and the more reactive monomer is fluoroacrylic acid. In polymerisation in DMSO the reactivities of the radicals and the monomers are similar. This is apparently associated with the formation of complexes between the polymer radicals and DMSO molecules, as suggested by Gal'perina et al.[72]

Table 10. The rate constants for chain propagation in the copolymerisation of acrylic (M_1) and fluoroacrylic (M_2) acids at 50°C.

Constant	Water	DMSO
r_1	0.5	0.5
r_2	1.5	0.7
k_{11}, litre mole^{-1} s^{-1}	47 600	1790
k_{22}, litre mole^{-1} s^{-1}	5 350	1950
k_{12}, litre mole^{-1} s^{-1}	95 200	3580
k_{21}, litre mole^{-1} s^{-1}	3 570	2790

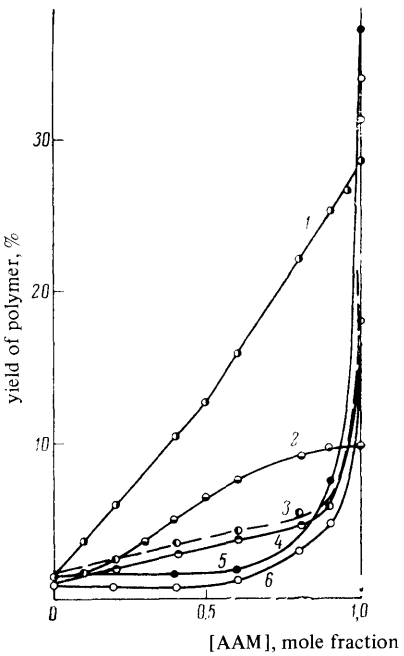


Figure 5. The influence of the composition of the initial mixture of monomers on the yield of copolymers of acrylamide and acrylonitrile in their radiation-induced copolymerisation in different solvents at 20°C; $[M_1] + [M_2] = 2.5$ M: 1) dioxan; 2) acetonitrile; 3) methanol; 4) dimethylformamide; 5) water; 6) acetic acid.

In the copolymerisation of methacrylic acid with acrylate and methacrylate esters (methyl acrylate, methyl methacrylate, and butyl methacrylate) in dioxan–water mixtures[88] an increase of the water content in the solvent leads to a decrease of the copolymerisation constant for the acid and an increase of that for the ester comonomer. The above data indicate a higher reactivity of the acid radical in water and are in good agreement with the ideas developed by Gal'perina et al.[72]

The formation of hydrogen bonds with the solvent also influences the reaction kinetics and the composition of the acrylamide–acrylonitrile copolymers[89]. In solutions in acetic acid, dimethylformamide, water, and methanol, i.e. solvents forming hydrogen bonds with acrylamide the addition of small amounts (up to 10%) of acrylonitrile to this monomer reduces the rate of the process significantly. In dioxan and acetonitrile the decrease of the rate of polymerisation following the addition of acrylonitrile is much smaller (Fig. 5). The greatest number of acrylamide units in the copolymer has been found in polymerisation in dioxan and acetonitrile. The copolymerisation constant for acrylamide depends little on the nature of the solvent (0.21–0.50), whereas for acrylonitrile the constant changes from 0.08–0.10 in acetonitrile and dioxan to 0.50 in acetic acid, 1.13 in methanol, and 1.9 in water and dimethylformamide. The observed effects are probably due to the different degrees of association of acrylamide molecules in the above solvents.

Table 11. Copolymerisation of acrylamide (M_1) with styrene in various solvents[90] ($\Delta\nu$, cm^{-1}, is the shift of the absorption bands).

Solvent	r_1	r_2	$\Delta\nu_{CO}$	$\Delta\nu_{NH^I}$	$\Delta\nu_{NH^{II}}$	$\Delta\nu_{NH,\,av}$
Benzene	12.5	0.25	1	15	10	12.5
o-Dichlorobenzene	12.5	0.25	3	5	5	5
Benzene–benzonitrile	4.4	1.5	8	46	45	45.5
Chloroform	—	—	13	47	55	51
Benzonitrile	2.4	1.35	12	70	55	62.5
Dioxan	1.38	1.27	10	205	170	187.5
Diglyme	1.09	1.40	10	190	206	198
Ethanol	0.30	1.44	13	205	230	217.5
Methoxyethoxyethanol	0.27	1.66	22	205	230	217.5
Water–t-butyl alcohol	0.78	2.93	28	205	230	217.5
DMSO	0.16	2.01	17	245	235	240
DMSO	0.43*	2.0*	—	—	—	—
Methanol	0.20	1.05	13	205	230	217.5
Pyridine *N*-oxide	—	—	9	65	90	77.5
Tetrahydrofuran*	0.62	1.1	—	—	—	—

*Gromov's data[21].

The copolymerisation of acrylamide with styrene in a large number of solvents of different types has been investigated[90]. The solvents selected were compounds which influence the acrylamide structure by the formation of hydrogen bonds, by dipole–dipole interaction, or by both factors. The change in the structure of acrylamide was inferred from the shift of the infrared absorption bands characterising the NH_2 or C=O groups. Thus the formation of hydrogen bonds between the monomer and the solvents as well as the polar interaction between them induce a change in the electron density around the double bond of acrylamide and hence alter its reactivity. The relatively low dipole moment as well as the inertness of styrene molecules with respect to the formation of hydrogen bonds entail a virtual constancy of the reactivity of this monomer as well as its radical in different solvents. The data presented in Table 11 show that the copolymerisation constant for acrylamide changes significantly in different solvents as $\Delta\nu_{NH}$ is altered. In solvents where neither dipole–dipole

interactions nor the formation of hydrogen bonds with acrylamide are observed (benzene, dichlorobenzene) the resulting copolymer is enriched in the acrylamide component. In those cases where the acrylamide molecules form strong hydrogen bonds with the solvent or are actively involved in a dipole–dipole interaction the copolymers are enriched in styrene.

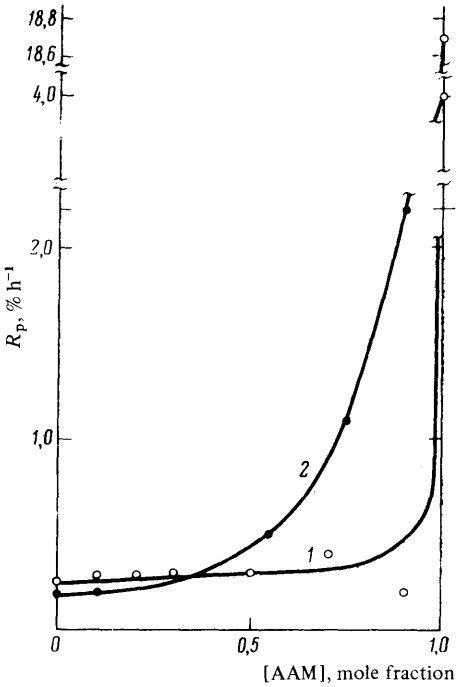


Figure 6. Dependence of the rate of copolymerisation of acrylamide with styrene on the composition of the initial mixture in DMSO (curve *1*) and THF (curve *2*); $[M_1]+[M_2] = 2.0 - 2.7$ M; initiator concentration $(5.3-6.5) \times 10^{-3}$ M; 40°C.

The nature of the solvent also influences the kinetics of the copolymerisation of acrylamide with styrene[22]. Fig. 6 shows that the addition of 10 mole % of styrene decreases the initial rate of reaction relative to the rate of the separate polymerisation of acrylamide, by a factor of approximately two in solution in tetrahydrofuran and by a factor of 50–60 in solution in DMSO. An even greater change in the rate of polymerisation is observed when the reaction is carried out in water. Thus the addition of even 0.01 mole % of styrene reduces the rate of reaction by a factor of 1.5–2.5, while the rate of polymerisation of a mixture of monomers containing 6 mole % of styrene is smaller by a factor of approximately 100 than the rate of homopolymerisation of acrylamide. The copolymers are in all cases enriched in styrene, the degree of enrichment being greater in DMSO and formamide than in tetrahydrofuran. The copolymer formed in water on copolymerisation of 94 mole % of acrylamide (AAM) and 6 mole % of styrene is virtually pure polystyrene. The copolymerisation constants for this pair of monomers are r_1(AAM) = 0.43 and $r_2 = 2.0$ in DMSO and $r_1 = 0.62$ and $r_2 = 1.1$ in tetrahydrofuran.

In conformity with the known characteristics of radical copolymerisation, the results obtained[22] indicate different reactivities of the acrylamide radical in the solvents investigated: the reactivity is highest in water and lowest in tetrahydrofuran, which agrees with the rates of separate polymerisation of acrylamide in the above solvents[54]. These results can be accounted for, as in Gal'perina's study[23], by the formation of complexes between the solvent and the polymer radical.

The different degrees of dimerisation of acrylamide and acrylic acid molecules as a result of hydrogen bonding with the solvent are responsible for the difference between the copolymerisation constants for the above monomers in water and acetone. r_1(AAM) = 1.38 and $r_2 = 0.36$ for the copolymerisation in acetone, while in aqueous solution $r_1 = 0.60$ and $r_2 = 0.43$.[91,92] These values indicate that the formation of hydrogen bonds between the monomeric molecules has a greater effect on the reactivity of acrylamide than on that of acrylic acid, since the transition from the associated form of acrylamide (in acetone) to the non-associated form (in water) is accompanied by a greater increase of the reactivity of the acrylamide radical compared with that of acrylic acid. Data[93] for the copolymerisation of acrylamide with acrylic and methacrylic acids in solvents of different polarity (dioxan, dioxan–ethylene glycol, and chloroform–ethanol), according to which an increase of solvent polarity entails a decrease of the copolymerisation constant for acrylamide, lead to the same conclusion.

Table 12. Copolymerisation of acrylamide and its derivatives (M_1) with styrene (St) and methyl methacrylate (MMA) in various solvents[95–99].

Solvent	St		MMA		Solvent	St		MMA	
	r_1	r_2	r_1	r_2		r_1	r_2	r_1	r_2
Acrylamide					**Dimethylacrylamide**				
Dioxan	1.38	1.27	2.45	2.55	Dioxan	0.44	1.28	0.51	2.04
Dioxan + ethanol (70:30 by volume)	0.59	1.13	0.82	2.53	Ethanol	0.42	1.33	0.42	2.30
Ethanol	0.30	1.44	0.44	2.60	Toluene	0.23	1.23	0.45	1.80
Diacetoneacrylamide					**Methacrylamide**				
Dioxan	0.47	1.85	0.50	1.80	Dioxan	1.29	1.46	1.27	1.55
Ethanol	0.30	1.80	0.31	2.00	Ethanol	0.54	1.27	0.43	1.68
Benzene	0.49	1.77	0.57	1.68					
Ethyl acetate	0.49	1.70	0.46	1.70					
					***N*-Methylacrylamide**				
					Dioxan	0.64	2.10	1.03	3.50
					Ethanol	0.20	2.20	0.28	3.30

These results conflict with data for the copolymerisation of acrylamide with methyl methacrylate published by Jacob et al.,[94] who showed that the addition of water to DMSO or chloroform increases significantly the content of acrylamide units in the copolymer and correspondingly the copolymerisation constant for acrylamide:

Solvent	DMSO	DMSO + H_2O (9:1)	Chloroform	Chloroform + 1% H_2O
r_{AMM}	0.2	1.0	1.0	3.5

The addition of water has virtually no influence on the copolymerisation constant for methyl methacrylate in both cases. Unfortunately no data are presented in the above communication[94] concerning the phase state of the reaction system and also the yields of the copolymers, so that it is difficult to account for the observed inconsistency with data obtained elsewhere[22,89,90].

The influence of hydrogen bonds between monomers and solvents on the reactivity of the former has been demonstrated particularly clearly in a series of studies[95–99]. The

copolymerisation constants for acrylamide, methacrylamide, *N*-methylacrylamide, and *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (diacetoneacrylamide) with methyl methacrylate or styrene depend on the nature of the solvent (dioxan, ethanol, and their mixtures), the effect being most pronounced for acrylamide and methacrylamide (Table 12). In the copolymerisation of *N*,*N*-dimethylacrylamide with styrene or methyl methacrylate the quantities r_1 and r_2 are virtually the same in different solvents (dioxan, toluene, ethanol, dimethylformamide, and ethyl acetate). The difference between the behaviour of these monomers is apparently associated with the fact that, whereas acrylamide, methacrylamide, *N*-methylacrylamide, and diacetoneacrylamide can exist in the form of dimers (which are partly or fully decomposed as a result of the formation of hydrogen bonds with solvent molecules, which alters their reactivity and hence influences the copolymerisation constants), *N*,*N*-dimethylacrylamide molecules do not dimerise. The data presented also show that the hydrogen bonds between the solvent and the carbonyl group of amides have almost no influence on the reactivity of the amides.

The influence of the solvent on the intermolecular association of monomer molecules evidently explains the results obtained in the copolymerisation of methacrylamide with styrene in different solvents. The addition of ethanol, dimethylformamide, and pyridine to the mixture of monomers lowers the proportion of methacrylamide units in the copolymer [100]. The copolymerisation constant for methacrylamide changes little in the copolymerisation in acetic acid, ethanol, dimethylformamide, and pyridine (0.30–0.50), while the copolymerisation constant for styrene increases on passing from acetic acid (0.65) to other solvents (1.4–1.8). It has been assumed [100] that, in copolymerisation in acetic acid, methacrylamide reacts in the form of dimers, since the stereochemistry and size of the amide group of the monomer and those of the carboxy-group of the acid differ appreciably.

Indeed, the compositions of the methacrylamide–styrene copolymers obtained in acetic acid (in the region of homogeneous copolymerisation) and in benzene, which does not form hydrogen bonds with methacrylamide and does not therefore decompose its dimers, are the same. As for acrylamide and acrylic and methacrylic acids, the formation of hydrogen bonds between methacrylamide and solvent molecules in other solvents causes the dimeric methacrylamide aggregates to dissociate; this alters the electron density at the double bond of the monomer and decreases the reactivity of the latter.

The influence of the solvent on the copolymerisation of monomers of low polarity is much less marked, as in their separate polymerisation. Thus, in the copolymerisation of styrene (M_1) with methyl methacrylate at 60°C in benzene solution [48], the values of r_i are as follows: $r_1 = 0.57$ and $r_2 = 0.46$, whereas in phenol $r_1 = r_2 = 1.35$. A slight change in the reactivity of polymer radicals, which alters r_1 and r_2, has also been observed in the copolymerisation of cyclododecyl or cyclohexyl acrylate with acrylonitrile in solution in benzene, dioxan, and tetrahydrofuran. When styrene instead of acrylonitrile is used as the second comonomer, the solvent has no influence [101].

V. CONCLUSION

The above discussion shows that a definite influence of the nature of the solvent on the rates of polymer chain propagation and termination reactions under the conditions of radical polymerisation has now been established. Whereas in the case of weakly polar monomers the role of the solvent is largely manifested to only a slight extent, for polar monomers (acrylamide, acrylic acids, and *N*-vinylpyrrolidinone) an appreciable variation in the constant k_p is observed in solvents of different types.

The observed variation of k_p due to the different reactivities of the polymer radicals in different solvents is associated with different kinds of specific interactions between the reacting species and solvent molecules (donor–acceptor interaction, the formation of π-complexes, and hydrogen bonding). In the few studies dealing with the temperature dependence of the rates of the elementary chain propagation reactions it was shown that the variation of k_p is caused by the change in the activation energy for this reaction.

In the polymerisation of weakly polar monomers (particularly styrene) the relatively weak donor–acceptor interaction between the components of the reaction system apparently plays the main role. The solvent effect is therefore comparatively slight in this instance. The particularly marked differences observed in the polymerisation of water-soluble monomers in water, on the one hand, and in organic solvents, on the other, are probably associated both with the presence of hydrogen bonds between the reacting species and solvent molecules and with the formation of π-complexes between the solvent and the growing radicals.

Unfortunately, there are not yet any direct experimental literature data permitting the determination in each specific case of the type of interaction between the reacting species and solvent molecules, which determines the observed influence of the solvent. The claim that different kinds of complexes are formed between the components of the reaction mixture is merely tentative. The formation of such complexes has been demonstrated in only a few instances. Evidently further study should be directed towards the experimental determination of the constants k_p and k_t and the corresponding activation energies for other monomers in different solvents and their mixtures as well as towards the elucidation of the detailed mechanism of the influence of solvents.

Furthermore, it is quite likely that the influence of the solvent on k_p and k_t in radical polymerisation is also caused by a change in the conformation of the polymer radicals as a function of the nature of the medium. A clear relation has been established between the rates of polymerisation of monomeric electrolytes (acrylic acids, β-betaine) and the conformational state of the macromolecules. The rates of polymerisation and viscosities of polymer solutions vary in parallel as a function of the pH of the medium and the salt concentration in solution [8].

The polymerisation of acrylamide in the DMSO–water binary solvent has been investigated recently and an increase of the overall rate of reaction and of the molecular weight of the polymers with increasing water content in the solvent has been demonstrated. It has also been shown (on the basis of viscosity data) that the effective size of the macromolecular coils increases with increasing water content in the solvent. It is suggested that the influence of solvent composition on the rate of reaction is caused by a change in the local concentration of monomer molecules in the coils containing polymer radicals [102].

The recently published studies [103,104], where the constants k_p and k_t have been determined for the first time for the polymerisation of acrylamide in binary solvents, are significant. In DMSO–water mixtures the overall rate of reaction ($k_p/k_t^{1/2}$) and the constant k_p change sharply following the addition of even small amounts of DMSO and

then decrease more smoothly (Fig. 7). The constant k_t passes through a minimum as a function of solvent composition, corresponding to the maximum solvent viscosity (Fig. 7). In mixtures of water with dioxan and tetrahydrofuran having the same composition the quantities $k_p/k_t^{1/2}$ and k_p give rise to the sequence DMSO < dioxan < tetrahydrofuran, i.e. the same as in the polymerisation of acrylamide in one-component solvents [22,54,58].

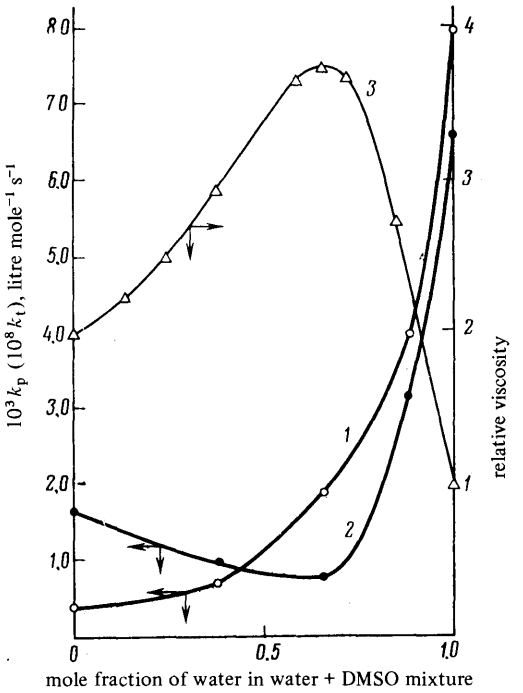


Figure 7. Dependence of k_p (curve *1*) and k_t (curve *2*) for the polymerisation of acrylamide in a water–DMSO mixture at 30°C and of solvent viscosity (curve *3*) on solvent composition.

The results [103,104] have been examined on the basis of the idea of complex formation between the growing radicals and solvent molecules. Furthermore, a correspondence has been demonstrated between the constants k_p and the intrinsic viscosities of the polymers in the solvents investigated; it is suggested that the influence of the solvent may be due to the different dimensions of the growing macroradical coils [104].

Thus, when the causes responsible for the influence of the solvent on k_p and k_t in radical polymerisation are examined, account must be taken of at least two factors:

1. The formation of complexes of different kinds by the reacting species with one another and with solvent molecules.

2. The state of the polymer coils (their dimensions) containing macroradicals and the dependence of this state on the nature of the reaction medium (solvent). Here the results of more detailed studies, for example, of the determination of the concentration of the monomer in the coil near the growing end of the polymer chain, are significant.

The contribution of each of these factors to the overall effect is at present obscure. It is probably different for different monomers and solvents.

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Inorganic Radical-ions and Their Organic Reactions

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A systematic account is given of the available information about the simplest inorganic radical-ions O_2^-, O^-, O_3^-, CO_2^-, SO_4^-, etc., their reactions with organic substrates are considered, and their possible role in organic reactions is discussed. The bibliography includes 381 references.

CONTENTS

I.	Introduction	1055
II.	The radical-anion of molecular oxygen	1055
III.	Other oxygen radical-anions	1065
IV.	The carbon dioxide radical-anion	1066
V.	The SO_4^- radical-anion	1067
VI.	Other inorganic radical-ions	1069

I. INTRODUCTION

The salt-like derivatives of the radical-anion of molecular oxygen became known long before their true nature could be understood. Thus potassium superoxide $K^+O_2^-$ was described by Thenard and Gay-Lussac[1] as early as 1811. It would seem that the idea of the ability of the oxygen molecule to capture a single electron should have arisen for the first time in the study of the mechanism of the oxidation by oxygen, but in reality it was formulated by Bodenstein[2], who discovered the chain mechanism of the interaction of hydrogen with chlorine. Assuming initially that free electrons participate in chain initiation, Bodenstein explained the inhibiting activity of oxygen by the ability of its molecule to capture a single electron, i.e.

$$O_2 + e \rightarrow O_2^- .$$

Heavy alkali metals react with oxygen to form a large number of compounds, among which the "superoxides" MO_2 have been most thoroughly studied in the course of many years[3,4].

There is a striking contrast between the universal distribution of the radical-anion O_2^- in living nature and the small amount of information available about its reactions with organic compounds. However, in recent years a number of unusual reactions of this type were discovered. It was established that the adsorption of oxygen on various metal oxides is accompanied by the formation of the radical-anions O_2^-, O^- and O_3^-.[5] The available data suggest that the adsorbed oxygen radical-anions are responsible for the heterogeneous-catalytic oxidation of various substances by oxygen[5,6]. The formation of the radical-anion CO_2^- may be the first stage in the fixation of carbon dioxide in photosynthesis[7]. Data obtained in a study of the EPR spectra of inorganic radical-anions have been surveyed[8].

The available information about inorganic radical-anions is scattered throughout journals devoted to inorganic, analytical, organic, and physical chemistry, electrochemistry, and biochemistry. Without claiming to cover this field exhaustively, we attempted to compile the most important results obtained in these hitherto divergent disciplines and to deduce possible generalisations.

II. THE RADICAL-ANION OF MOLECULAR OXYGEN

1. Methods of Preparation and Physicochemical Properties

Molecular oxygen has a significant positive electron affinity (0.87 ± 0.13 eV);[9] for this reason, the principal methods for the preparation of superoxide compounds involve the reduction of oxygen. Potassium, rubidium, and caesium superoxides are formed on combustion of these metals in air or in oxygen[10-13]. On combustion, sodium forms a peroxide, since sodium superoxide is thermally unstable and decomposes even at 80–90°C into sodium peroxide and oxygen[14]. The converse reaction takes place at a higher pressure and is used as an industrial method for the preparation of NaO_2.[15]

Among superoxides with ionic structures, the lowest stability is shown by lithium and alkaline earth metal superoxides, which are obtained by ozonising the peroxides of these metals at low temperatures[16,17]. Barium peroxide is stable only below −50°C.[17]

The superoxide radical-anion (SORA), which is short-lived in aqueous solutions, is generated when molecular oxygen captures a hydrated electron[18]:

$$H_2O \xrightarrow{\nu} H^\cdot + {}^\cdot OH + e_{aq}^- + H^+ ,$$

$$H^\cdot + O_2 \rightarrow O_2^- + H^+ ,$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \ (k = 1.9 \cdot 10^{10} \text{ (litre mole}^{-1}\text{ s}^{-1}\text{)}).$$

The most convenient method for the synthesis of sodium and potassium superoxides on a preparative scale involves the reduction of oxygen by solutions of the metals (in liquid ammonia)[19,20] or by ketyls, for example, sodiobenzophenone in tetrahydrofuran[21,22]:

$$Ph_2CO^-Na^+ + O_2 \rightarrow Ph_2CO + NaO_2 .$$

Tetramethyl- and tetraethyl-ammonium superoxides can be obtained by the double decomposition reaction between KO_2 and the corresponding tetraalkylammonium hydroxide[23-25]. In order to obtain Me_4NO_2, tetramethylammonium fluoride can be used instead of tetramethylammonium hydroxide[23]; tetraalkylammonium superoxides can be extracted with liquid ammonia:

$$R_4NX + KO_2 \rightarrow R_4NO_2 + KX ;$$
R=Me or Et; X=OH or F .

Tetramethyl- and tetraethyl-ammonium superoxides are yellow substances melting at 97°[23] and 50°C[25] respectively. In contrast to the thermally stable potassium, rubidium, and caesium superoxides, tetraalkylammonium superoxides decompose vigorously already at 100°C.[23,24]

Convenient methods for the preparative electrochemical reduction of molecular oxygen in aprotic media, leading to the formation of solutions of tetraalkylammonium superoxides, have been developed in recent years[26-31]. A solution of a supporting electrolyte R_4NX in an aprotic solvent (dimethylformamide, dimethyl sulphoxide, pyridine, and acetonitrile) is usually electrolysed at a controlled potential (−1.0 V) in a stream of gaseous oxygen; mercury, platinum, and gold cathodes are used. The resulting coloured solutions give rise to an EPR signal at a low temperature corresponding to the SORA.[26,27,30] It has been shown[32] that the SORA is generated also in the one-electron oxidation of hydrogen peroxide by an alkaline solution of sodium periodate.

Alkali metal superoxides are sparingly soluble in organic solvents. Incidentally, the solubility of KO_2 in dimethyl sulphoxide is sufficient for the measurement of EPR spectra[33]. The low solubility of alkali metal superoxides for a long time inhibited the investigation of their organic reactions. The situation changed significantly after the development of methods for the synthesis of tetraalkyl-ammonium superoxides, which are soluble in aprotic solvents, and also after the discovery in 1975 of the ability of potassium superoxide to dissolve in dimethyl sulphoxide[34] and even in benzene[35] in the presence of crown-ethers.

The crystal lattice of KO_2 is made up of regularly alternating K^+ and O_2^- ions, as in potassium chloride[15]. NaO_2 has a cubic face-centred lattice of the pyrite type[36]. The bond length in the O_2^- radical-anion is 1.29 Å.[37]

The conjugate acid of the SORA as a base is the free hydroperoxy-radical:

$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^- \quad .$$

This radical is a fairly strong acid (pK_a = 4.45,[38] 4.5,[39] 4.88[40]); thus the hydroperoxy-radical exists preferentially in the form of the SORA even in weakly acid media.

2. Chemical Properties

In aqueous solutions alkali metal and tetraalkylammonium superoxides are unstable and rapidly disproportionate to hydrogen peroxide and oxygen[41]:

$$2MO_2 + 2H_2O \rightarrow H_2O_2 + O_2 + 2MOH \ .$$

On passing to strongly alkaline solutions, the rate of disproportionation is greatly reduced[42]. A KO_2 solution in 8 M KOH obtained at −50°C gives rise to the EPR signal of the O_2^- radical-ion[43]. (It is of interest that KO_2 does not react with a solution of hydrogen chloride in dry ether even at room temperature[44].)

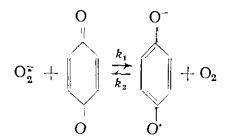
Despite the apparent simplicity of its electronic structure, the radical-anion O_2^- exhibits a varied and in many respects contradictory reactivity. At any rate the widely held view that superoxides with ionic structures can allegedly behave only as strong oxidants has since proved to be clearly untenable.

As a result of its intermediate position in the redox triad

$$O_2 \underset{-e}{\overset{+e}{\rightleftarrows}} O_2^- \underset{-e}{\overset{+e}{\rightleftarrows}} O_2^{2-}$$

the SORA exhibits a dual reactivity: depending on the nature of the substrate, it can behave both as an electron donor and an electron acceptor.

Studies in recent years have shown that the SORA can give up one electron to tetracyanoquinodimethane (TCQ),[33] quinones[45-49], and mono- and di-nitrobenzenes[33,50], converting them into radical-anions (detected by EPR):



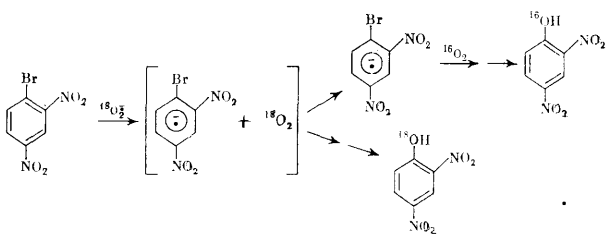
($k_1 = 1.1 \cdot 10^9$ litre mole^{-1} s^{-1}, $k_2 = 10^7$ litre mole^{-1} s^{-1} (Ref.47))

$$TCQ + O_2^- \xrightarrow{-O_2} TCQ^- \ ;$$

$$O_2^- + ArNO_2 \xrightarrow{-O_2} ArNO_2^- \quad .$$

The radical-anions of aromatic nitro-derivatives formed in this process undergo further reactions under the influence of oxygen (and also the excess of SORA); in particular, in the case of dinitrobenzenes one of the nitro-groups is replaced by a hydroxy-group[50].

When halogenonitro- and halogenodinitro-benzenes are acted upon by KO_2 in the presence of a crown-ether, halogen atoms are replaced by hydroxy-groups[50]. It is believed[50] that the first stage in these reactions is not classical nucleophilic substitution, but electron transfer from the SORA to the halogenonitro-derivatives, accompanied by further reactions of the resulting halogenonitrobenzene radical-anions under the influence of oxygen. Owing to the rapid reaction of oxygen, the formation of radical-anions could be demonstrated with the aid of EPR only in the case of *m*-bromonitrobenzene. The one-electron mechanism of the first stage is supported, in particular, by the interaction of $K^{18}O_2$ with 2,4-dinitrobenzene in a solution saturated with $^{16}O_2$. Less than 10% of the resulting 2,4-dinitrophenol contained the ^{18}O isotope[50]:



The reactivity of halogeno-2,4-dinitrobenzenes with respect to KO_2 diminishes in the sequence F > Br ≃ I > Cl,[50] while the sequence F > Cl ≃ Br ≃ I is characteristic of nucleophilic substitution reactions[51].

The fact that the interaction of halogenonitrobenzene radical-anions with oxygen can lead to nitrophenols follows also from kinetic data for the reaction of *p*-chloronitrobenzene with sodium methoxide in the presence of oxygen[52].

An interesting reaction has been observed in a study[33] where it was shown by EPR that treatment of *p*-nitrotoluene with KO_2 leads to the formation of the radical-anion of *p*-nitrobenzaldehyde, which is apparently a product of further reactions of the *p*-nitrotoluene radical-anion in the presence of oxygen and an excess of KO_2.

Among other reactions of the SORA as a one-electron reductant, one may mention the reduction of ferricytochrome *c* to ferrocytochrome *c*,[29] of Nitrotetrazolium Blue

to the corresponding formazan[53], and of tetranitromethane to the nitroformate anion[29,39].

The conjugate acid of the SORA (the $HO_2^{\cdot}$ radical) is a weaker electron donor than the SORA itself[39]:

$$O_2^{\cdot-} + C(NO_2)_4 \rightarrow {}^{-}C(NO_2)_3 + NO_2 + O_2 ,$$
$$(k = 1.9 \cdot 10^9 \text{ (litre mole}^{-1}\text{)},$$
$$HO_2^{\cdot} + C(NO_2)_4 \rightarrow {}^{-}C(NO_2)_3 + NO_2 + H^+ + O_2 ,$$
$$(k < 1.9 \cdot 10^5 \text{ (litre mole}^{-1}\text{ s}^{-1}\text{)}).$$

The interaction of the SORA with alkyl halides (tosylates) leads mainly to alkyl peroxides[54-59]. A three-stage reaction mechanism, in which the first stage is bimolecular nucleophilic substitution involving the SORA as the nucleophile, has been proposed[51,52,55]:

$$RX + O_2^{\cdot-} \rightarrow ROO^{\cdot} + X^- ,$$
$$ROO^{\cdot} + O_2^{\cdot-} \rightarrow ROO^- + O_2 ,$$
$$ROO^- + RX \rightarrow ROOR + X^-$$
$$X = Hal, \text{ or } p\text{-}CH_3C_6H_4SO_3-.$$

The above conclusion is based on the inversion of the configuration of the carbon atom linked to the halogen (the tosyl group) in the reaction of KO_2 with optically active halides or tosylates[55,60]. In addition, the sequence of the reactivities of the alkyl halides is the same as in the usual reactions of the S_N2 type (primary > secondary > tertiary; I > Br > Cl).[55,60,61]

The formal S_N2 mechanism does not rule out the possibility of one-electron transfer as one of the stages in the overall reaction[62,63]. In this connection the hypothesis[59] that the initial stage of the reaction under consideration is the reduction of the halide has attracted attention:

$$RHal + O_2^{\cdot-} \rightarrow [Hal^- \cdots R^{\cdot} \cdots O_2] \rightarrow RO_2^{\cdot} + Hal^- .$$

This mechanism is quite probable, since, as stated above, the SORA is a fairly effective electron donor and organic halides are capable of accepting an electron (see, for example, Refs. 64–68). The inversion of the configuration is in this case determined solely by the direction of attack on RHal from the side opposite to that of the halogen.

The formation of alcohols[60] as the main products of the reaction of alkyl halides (tosylates) with KO_2 in dimethyl sulphoxide takes place with participation of the solvent[59]. The ROO^- ion, formed "normally", reacts with dimethyl sulphoxide faster than with RX:

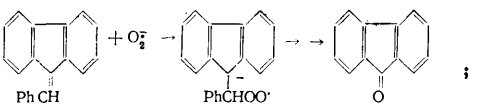
$$ROO^- + Me_2SO \rightarrow MeS(O^-)Me(OOR) \rightarrow Me_2SO_2 + RO^- .$$

An analogous reaction of the anion of triphenylmethyl hydroperoxide, leading to triphenylmethanol, has been observed[69].

The cleavage of tosylates and methanesulphonates to the corresponding alcohols on treatment with KO_2 in dimethyl sulphoxide, which takes place with complete inversion of the configuration at the carbon atom and which constitutes a synthetic chain procedure in the chemistry of prostaglandins[70,71], apparently also involves the interaction of the corresponding hydroperoxy-anions with dimethyl sulphoxide.

Acid anhydrides[54] and chlorides[44,55,72] are converted into acyl peroxides in high yields on treatment with KO_2, the reaction occuring in a non-aqueous medium. In contrast to the reactions of KO_2 with alkyl and acyl halides, only hexamethyldisiloxane is formed in a high yield by the reaction of chlorotrimethylsilane and KO_2.[44]

The initial nucleophilic addition of the SORA has been postulated in its reactions with benzylidenefluorenone[55] and esters[73,74]:



This mechanism is supported by the finding that, when the acetate derived from (-)(*R*)-2-octanol is cleaved, the configuration of the chiral carbon atom is almost completely preserved[73].

Despite the fact that the electrochemical reduction of the SORA to the O_2^{2-} anion is well known[28,75], there have been so far no studies in which the analogous reaction under the influence of chemical electron donors (DH), i.e. a reaction of the type

$$DH + O_2^{\cdot-} \rightarrow DH^{+\cdot} + O_2^{2-}$$

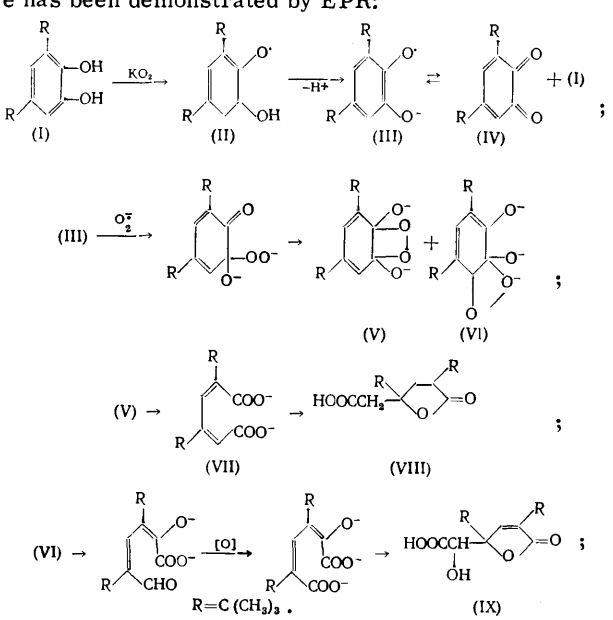
was clearly identified.

The study of reactions of this kind is significantly complicated by the fact that the electron transfer stage is masked by the subsequent rapid processes. For example, electron transfer should be accompanied in certain cases by the recombination or abstraction of a proton under the influence of O_2^{2-}:

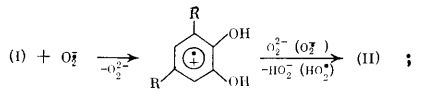
$$DH^+ + O_2^{2-} \rightarrow DHO_2^- ;$$
$$DH^+ + O_2^{2-}(O_2^{\cdot-}) \rightarrow D^{\cdot} + HO_2^-(HO_2^{\cdot}) .$$

Whereas in the first example the overall result of the reaction is the addition of the SORA to the substrate ($DH + O_2^{\cdot-} \rightarrow DHO_2^-$), the second example can be formally classified as a reaction of the S_H2 type ($DH + O_2^{\cdot-} \rightarrow D + HO_2^-$), i.e. one involving the abstraction of a hydrogen atom.

On treatment with KO_2, 3,5-di-t-butylcatechol (I) is converted largely into a mixture of 3,5-di-t-butyl-*o*-benzoquinone (IV) and compounds (VIII) and (IX).[76] The presence of the radical-anions (III) in the reaction mixture has been demonstrated by EPR:[77]



The intermediate relatively unstable diacid (VII) was isolated on a preparative scale in a low yield[77]. It is extremely likely that the first stage of the process actually consists of two such reactions:



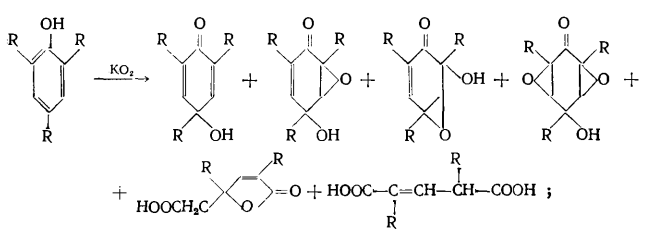
R = C(CH$_3$)$_3$.

Indeed, the abstraction of a hydrogen atom from phenols under the influence of various oxidants is preceded by a stage involving electron transfer from the phenol molecule to the oxidant accompanied by rapid deprotonation of the phenol radical-cation formed[78]. A similar mechanism has been adopted for the abstraction of a hydrogen atom from aliphatic alcohols under the influence of the $SO_4^{\cdot-}$ radical-anion[79,80].

It is of interest to note that the oxidation of alkaline solutions of the catechol (I) by oxygen also leads to *o*-quinone (IV);[81] furthermore, under appropriate conditions the formation of compound (VIII) is also actually possible[82]. Apparently the similarity of the products of the reactions of polyhydric alcohols with oxygen and the SORA is associated with the fact that the SORA is involved in reactions where polyhydric phenols are oxidised by molecular oxygen. The above view is consistent with the data of a number of investigations[83-87], where the ability of polyhydric alcohols to reduce oxygen in the presence of bases was pointed out.

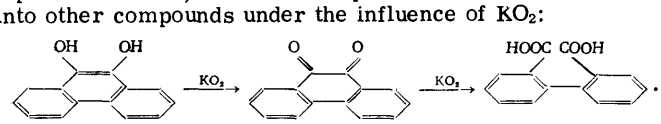
The oxidation of the catechol (I) by atmospheric oxygen in the presence of copper(I) chloride leads to *cis,cis*-di-t-butylmuconic acid[88], which, as stated previously, is also formed on oxidation of the above catechol derivative by KO_2.[73] In this case there is a preliminary activation of oxygen by the formation of its complex with Cu_2Cl_2, in which the reactivity of the dioxygen group in relation to the catechol (I) is probably similar to that of $O_2^{\cdot-}$ in KO_2.

Treatment of 2,4,6-tri-t-butylphenol with potassium superoxide in the presence of 18-crown-6-ether leads to a very complex mixture of products[89]:



R=C(CH$_3$)$_3$.

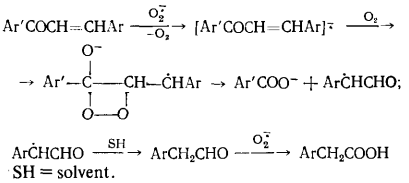
The oxidation of 9,10-dihydroxyphenanthrene under the influence of KO_2 leads to 9,10-phenanthrenequinone and diphenic acid[54,76], which is incapable of further conversion into other compounds under the influence of KO_2:



The cleavage of the fragment –CO–CO– is a fairly general reaction of the SORA and usually leads to carboxylic acids in high yields[54,90,91]. Although San Filippo et al.[91], who investigated the reaction of KO_2 with benzil and its derivatives, speak of the oxidative cleavage of benzils by KO_2, this evidently applies only to the final result, since it is more likely that the reaction actually begins with electron transfer from the SORA to benzil:

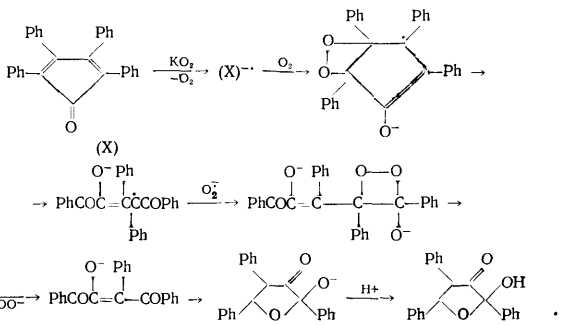


A similar mechanism has been adopted for the cleavage of chalcones[92]:

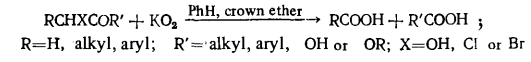


It has been shown in separate experiments that, on reaction with KO_2, aldehydes can be indeed converted into the corresponding carboxylic acids[54,92].

On treatment with potassium superoxide, tetracyclone (X) is smoothly converted into 2-hydroxy-2,4,5-triphenyl-3-furanone[35,92]:



The cleavage of the C–C bond is also observed when various other carbonyl derivatives are acted upon by the SORA:[91]



It is seen from the examples presented that the SORA is capable of cleaving a very wide range of carbonyl compounds to form carboxylic acids.

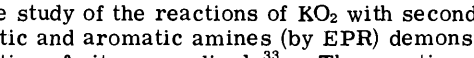
Consideration of the reactions of the SORA with organic substrates accompanied by the cleavage of C–C bonds shows that the key factor in all such reactions is apparently the formation of labile dioxetans, which are known to decompose readily to carbonyl compounds[93].

Ascorbic acid is readily dehydrogenated by the SORA to dehydroascorbic acid[94,95] ($k = 2.7 \times 10^5$ litre mole^{-1} s^{-1})[95].

When 9,10-dihydroanthracene, fluorene, and diphenylmethane are treated with the SORA, the methylene groups are oxidised to carbonyl groups[31,56]. These reactions probably proceed via the abstraction of hydrogen atoms from methylene groups by the superoxide radicals and subsequent transformations of the resulting diarylmethyl radicals under the influence of oxygen and the excess SORA. If the molecule contains an activated methylidyne fragment, then the final product is a hydroperoxide:



The study of the reactions of KO_2 with secondary aliphatic and aromatic amines (by EPR) demonstrated the formation of nitroxy-radicals[33]. The reaction also takes place in the absence of molecular oxygen:



Secondary alcohols (isopropyl alcohol and diphenylmethanol) are oxidised by NaO_2 to ketones (the yields of acetone and benzophenone are 33 and 55% respectively)[96].

It has been found[97] that the SORA is capable of abstracting a hydrogen atom from cysteine; the hydroperoxy radical is not involved in this reaction:

$$RSH + O_2^- \xrightarrow[-HO_2^-]{} RS^\cdot$$

RSH = cysteine.

Under the usual conditions, the reaction of KO_2 with phenylhydrazine in the presence of dicyclohexyl-18-crown-6-ether can serve as a source of phenyl radicals[98]:

$$PhNHNH_2 \xrightarrow{O_2^-} PhN{=}NH \xrightarrow[-HO_2^-]{O_2^-} Ph^\cdot + N_2;$$

$$Ph^\cdot + PhN{=}NH \xrightarrow{-PhH} Ph^\cdot + N_2 \ ;$$

$$Ph^\cdot + PhH \rightarrow \rightarrow Ph{-}Ph \ .$$

On oxidation of other compounds with an N–N bond under the same conditions, the following products are formed[98] (the yields expressed as percentages are indicated in brackets): toluene (54), benzoic acid (15), benzyl alcohol (6), and benzaldehyde (6) from benzylhydrazine; n-octane (32) from n-octylhydrazine; *N*-nitrosodiphenylamine (50) from 1,1-diphenylhydrazine; *N*-methyl-*N*-nitroaniline (33) from 1-methyl-1-phenylhydrazine; azobenzene (98) from 1,2-diphenylhydrazine; benzophenone azine (83) from benzophenone hydrazone; fluorenone (86) from 9-diazofluorene. Many of these reactions apparently begin with the state involving the abstraction of a hydrogen atom from the substrate.

Summarising the foregoing findings, one should note that reactions where the SORA plays the role of a mild reductant, a moderately strong nucleophile, or a free radical exhibiting a moderate dehydrogenating activity are the most characteristic of this species. An interesting feature of the SORA is its ability to react with both π-electron deficient systems (aromatic nitro-compounds) and with compounds having an excess of π electrons (phenols) as well as nucleophiles of the amine type.

3. Reactions Involving the Intermediate Formation of the SORA

Having adopted the view that, after the preliminary binding of the reacting species in complexes, the displacements of the atomic nuclei relative to one another are usually preceded by electron transfer[63], the oxidation of various compounds by oxygen can be represented by the following scheme:

$$RH + O_2 \rightleftarrows RH \cdots O_2 \rightleftarrows [RH^{+\cdot} \cdots O_2^-] \quad (XI);$$

$$(\text{or } [R^\cdot \cdots H^+ \cdots O_2^-]) \rightarrow R^\cdot + HO_2^\cdot \ .$$

In particular, the results of studies on the kinetics of the oxidation of *o*-xylene by oxygen are treated in this way[99]. In this interpretation of the mechanism of the oxidation reaction the tendency towards an increase of the ease of oxidation of organic compounds by oxygen accompanied by an increase of their capacity for electron transfer, which is usually observed, can be naturally accounted for.

Electron transfer to the charge-transfer complex (CTC) (XI) can apparently be induced also by the irradiation of the RH–O_2 system by light whose wavelength corresponds to the absorption band of the charge-transfer process[100–102], for example[102]:

$$C_2H_5OH \cdots O_2 \xrightarrow{h\nu} [C_2H_5\dot{O}H \cdots O_2^{-\cdot}] \rightarrow \text{oxidation products.}$$

One of the types of reactions in which there is a possibility of the formation of the SORA is that of neutral free radicals with oxygen. Thus it has been noted[103] that the radical obtained in the one-electron reduction of the oxidised form of nicotinamide-adenine dinucleotide (NAD^+) in aqueous solutions is much less stable in the presence of oxygen than in its absence. This can be explained by the occurrence of the process

$$NAD^\cdot + O_2 \rightarrow NAD^+ + O_2^- \ (k = 1.9 \times 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}),$$

apparently accompanied by the decomposition of the resulting SORA under the influence of water.

It is extremely interesting that the rate of reaction with oxygen increases in parallel with the enhancement of the reducing properties of the radical in the sequence $^\cdot CH_2CMe_2OH \simeq {}^\cdot CH_2CH(Me)OH < {}^\cdot CH_2OH < (Me)_2{}^\cdot COH < {}^\cdot COOH$.[104] One of the possible explanations of this behaviour is electron transfer[104]:

$$R^\cdot + O_2 \rightarrow [R^+ \cdots O_2^-] \rightarrow RO_2^\cdot \ .$$

A fairly large number of examples characterising the ability of carbanions and cryptocarbanions to function as electron donors are available at the present time. Significant advances have been made in this field in recent years when it has been shown that this ability is exhibited in many fundamental reactions of organometallic chemistry[105]. The fundamental principle of the one-electron oxidation of carbanions by oxygen was formulated by Russell[69]:

$$R^- + O_2 \rightarrow R^\cdot \cdots O_2^- \begin{cases} \longrightarrow RO_2^- \\ \longrightarrow R^\cdot + O_2^- \end{cases};$$

$$R^\cdot + O_2 \rightarrow RO_2^\cdot \ ;$$

$$RO_2^\cdot + R^- \rightarrow RO_2^- + R^\cdot, \text{ etc.}$$

The formation of free radicals in reactions of organometallic compounds with oxygen has been reliably established[106–108]. Evidently electron transfer from the carbanion to oxygen must be preceded by the coordination of the oxygen atom to the metal atom[108]. A similar mechanism was adopted also for the oxidation with oxygen of various organometallic compounds having a covalent C–metal bond[108].

The oxidation of certain *O*-anions takes place similarly—with electron transfer to oxygen (see Section II, 6). The reaction of fused potassium, rubidium, and caesium hydroxides with oxygen at 410 °C leads to the formation of a mixture of the peroxide and superoxide of the corresponding metal[109]. According to McGrath's results[110], the Favorskii rearrangement includes a stage involving the one-electron reduction of oxygen by the alkali metal enolate.

The following mechanism, involving one-electron transfer from the anion R^-, has been proposed for the low-temperature oxidation of mercaptans by oxygen[111]:

$$RSH \rightleftarrows RS^- + H^+$$

$$RS^- + O_2 \rightarrow RS^\cdot + O_2^- \ ;$$

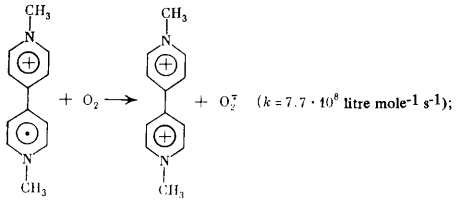
$$2RS^\cdot \rightarrow RSSR \ .$$

The participation of the SORA in the oxidation of mercaptans by oxygen has been demonstrated using a superoxide dismutase test[112] (see below).

It is of interest that, on passing from CH_3OH to tetrahydrofuran, dioxan, diglyme, and further to dimethylformamide, the rate of oxidation of butane-1-thiol increases by a factor of 334 in the presence of sodium methoxide. A possible explanation of this finding, postulating that the influence of the solvent is based on

the enhancement of the nucleophilic properties of CH_3O^- in the above sequence[111] is unconvincing because mercaptans are fairly strong acids and the change in the concentration of the thiolate anion on passing from methanol to dimethylformamide is hardly likely to cause such a large effect. The sharp acceleration of the reaction in highly solvating solvents is apparently associated with the significant decrease of the activation energy for electron transfer on passing from non-polar and weakly solvating media to polar and highly solvating media.

It has been shown by pulse radiolysis that the reaction of a radical-cation with oxygen in aqueous solution proceeds in two stages[113]:



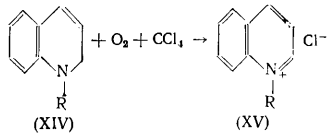
(XII) (XIII)

$(k = 7.7 \cdot 10^8$ litre mole^{-1} s^{-1});

(XII) + $O_2^{\cdot-}$ → (XIII) + O_2^{2-} $(k = 6.8 \cdot 10^8$ litre mole^{-1} s^{-1}).

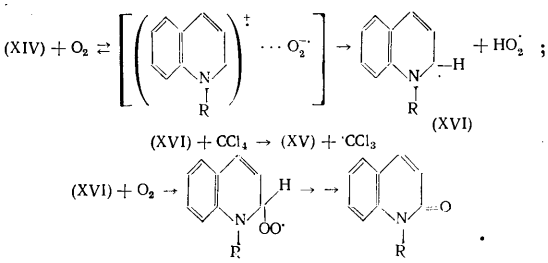
In methanol solution the reaction proceeds in a more complex manner [it is of second order with respect to (XII) and of first order with respect to oxygen][114].

In conformity with the results of kinetic studies, the involvement of the SORA in the oxidation by oxygen of certain aromatic amines in an aqueous medium has also been postulated[115]. An interesting reaction of 1,2-dihydroderivatives of quinoline with CCl_4, which proceeds only in the presence of oxygen and leads to quinolinium salts, has been described[116]:



(XIV) (XV)

The oxidation of dihydroquinolines in the absence of a solvent leads to the formation of the corresponding 2-quinolinones[116]. Analysis of literature data leads to the hypothesis that the above oxidation of 1,2-dihydroquinolines proceeds as follows:



(XVI)

(XVI) + CCl_4 → (XV) + $\cdot CCl_3$

Indeed, judging from polarographic reduction data, carbon tetrachloride is a fairly effective electron acceptor ($E_{1/2} = -0.25$ V relative to the saturated calomel electrode[117] in dimethylformamide as a solvent). It is to be expected that radicals of type (XVI) should be fairly strong reducing agents, since it is known, for example, that the radical $(CH_3)_2\dot{C}NH_2$, which contains the α-amino-group, is a strong reductant[118].

4. The Superoxide Radical-Anion and Singlet Oxygen (SO)

The hypothesis of the possible formation of oxygen in an excited state from the SORA has been put forward by Stauff et al.[119]

In a study of the hydrolysis of KO_2 in dimethyl sulphoxide in the presence of singlet oxygen acceptors Khan[120] concluded in 1970 that SO is formed in the disproportionation of the SORA:

$$2O_2^{\cdot-} + 2H^+ \rightarrow H_2O_2 + O_2(^1S).$$

Further investigations of a trapping of the SO formed in this reaction yielded contradictory results[33,121-124], which can be explained[125,126] by the rapid quenching of SO by the superoxide radical-anion, which competes with the capture of SO by the acceptors employed:

$$AO_2 \xleftarrow{A} O_2(^1S) \xrightarrow[-O_2^{\cdot-}]{O_2^{\cdot-}} O_2(^3S);$$

A = SO acceptor.

The mechanism of the formation of SO in the disproportionation of the SORA is still not clear, although one can assume that SO is formed in the one-electron oxidation of the SORA by its protonated form:

$$O_2^{\cdot-} + H\dot{O}_2 \rightarrow O_2(^1S) + HO_2^-,$$

since it has been shown that the oxidation of the SORA by strong one-electron oxidants leads to the formation of SO,[127] while in the reaction

$$2HOO^{\cdot} \rightarrow H_2O_2 + O_2$$

SO is not produced[128].

It is noteworthy that the reactions of dyes in an excited state (Dy^T) with molecular oxygen involving the conversion of the latter into SO, which formally reduce to energy transfer[129,130], can apparently proceed via an electron exchange mechanism with the intermediate formation of a radical-ion pair[131]:

$$Dy^T + O_2(^3S) \rightarrow [Dy^{\cdot+} \cdots O_2^{\cdot-}] \rightarrow Dy + O_2(^1S).$$

This is supported by the fact that the "annihilation" of oppositely charged radical-ions, responsible for the phenomenon of electrochemiluminescence[132], frequently results in the formation of electronically excited molecules:

$$Dy^{\cdot+} + A^{\cdot-} \rightarrow \begin{cases} \rightarrow Dy + A^* \\ \rightarrow Dy^* + A. \end{cases}$$

It has also been shown that the reaction of the SORA with certain radical-cations [the system of species belonging to the type forming the radical-ion pair $[Dy^{\cdot+} \ldots O_2^{\cdot-})$ leads to the formation of SO:[127]

$$Ferr^{\cdot+} + O_2^{\cdot-} \rightarrow Ferr + O_2(^1S);$$

Ferr = ferrocene.

The formation of radical-ion pairs $(Dy^{\cdot+} \ldots O_2^{\cdot-})$ in the reaction of dyes in triplet states has been postulated on the basis of kinetic data[133,134].

The transition of the dye molecules from the ground to the excited state can be accompanied by a sharp enhancement of the ability of the dye to function as an electron donor. It has been stated, for example, that the oxidation-reduction potential of the P_{700} pigment is +0.4 V in the ground state, while in the excited state it is −0.32 V (the sum $\Delta E_0 \simeq -0.7$ V!).[135]

5. "Covalent" Superoxides

The fact that many transition metal compounds which are effective reductants can be oxidised by oxygen naturally leads to the conclusion that the reaction

$$M^{n+} + O_2 \rightleftarrows M^{(n+1)+} + O_2^- .$$

is possible. This idea was apparently first formulated by Just[136], who investigated the oxidation of iron(II) salts by oxygen. Subsequently the idea of the involvement of the SORA in the oxidation of iron(II) via oxygen was developed by Weiss[137]:

$$Fe^{2+} + O_2 \rightleftarrows Fe^{3+} \cdot O_2^- \xrightarrow{H^+} Fe^{3+} + HO_2^\cdot \ ;$$
$$HO_2^\cdot + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \ ;$$
$$HO_2^- + H^+ \rightarrow H_2O_2 \ ;$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\cdot + OH^- .$$

In subsequent years the problem of the structure of the intermediate oxygen adducts $[MO_2]^{n+}$, formed in the oxidation of transition metal compounds by oxygen and considered by Weiss as SORA derivatives, was at the centre of attention. Some of these adducts are sufficiently stable to be isolated in the pure state. A number of reviews are devoted to the consideration of their properties[138–140]. The interest in oxygen adducts has been aroused mainly by the search for effective synthetic molecular oxygen transferring agents[138] and also by the search for methods of activating oxygen in various oxidation processes[141,142].

The studies in recent years have been characterised by the application of a wide variety of physical methods to the solution of the problem of the structure of metal compounds containing an oxygen molecule as a ligand. The latest advances in this field are discussed below.

In 1964 Weiss suggested that oxygen adducts formed by natural oxygen transferring agents (haemoglobin Hb and myoglobin Mb) should be regarded as iron(III) compounds containing the superoxide ion, i.e. $HbFe^{3+}\cdot O_2^-$ and $MbFe^{3+}\cdot O_2^-$.[143] In support of this hypothesis, Weiss referred particularly to the similarity of the ultraviolet spectra of these adducts and those of methaemoglobin and metmyoglobin derivatives and the fact that oxygen is "activated" in oxyhaemoglobin. Within the framework of Weiss's hypothesis, the diamagnetism of oxyhaemoglobin is explained by the antiferromagnetic interaction in the ion pair $HbFe^{3+}\cdot O_2^-$. Pauling[144] opposed this treatment, stating that oxyhaemoglobin should be regarded as an iron(II) derivative having the formula $HbFe^{2+}=O^+_{O^-}$. Quantum-mechanical calculations[145] support the view that the iron in $HbFeO_2$ is tervalent.

The formation of the $Fe-O_2$ bond in adducts of iron(II) compounds with oxygen can be represented by a correlation diagram (Fig. 1) within the framework of the molecular orbital method[146]. However, one should note that the diagram presented says nothing about the amount of ionic character of the $Fe-O_2$ bond.

The use of physical methods in the solution of the problem of the nature of the bond in oxyhaemoproteins yielded results which are not susceptible to a simple interpretation. Thus studies by the Mössbauer method showed that the chemical shifts of iron in haemoglobin and oxyhaemoglobin are approximately the same[147], which corresponds to approximately identical states of the iron in these compounds. On the other hand, the similarity of the Raman spectra of oxyhaemoglobin and methaemoglobin derivatives was interpreted as a result of the presence of iron(III) in $HbFeO_2$.[148,149] Furthermore, the vibration frequency of the O–O bond is 1107 cm^{-1} in $HbFeO_2$ [150] and 1145 cm^{-1} in KO_2,[151] while in gaseous oxygen it is 1555 cm^{-1}.[152] The study of oxyhaemoglobin by X-ray fluorescence spectroscopy led to the conclusion that there is an unpaired electron at the iron atom in oxyhaemoglobin[153].

The problem of the nature of the $Fe-O_2$ bond, particularly of the amount of its ionic character in oxyhaemoproteins, probably cannot be regarded as finally solved. One can only note that the antiferromagnetic interaction in oxyhaemoproteins, postulated in Weiss's hypothesis, is equivalent to the formation of a new electron pair, giving rise to the $Fe-O_2$ bond owing to the comparatively short $Fe-O_2$ distance, i.e. in fact it corresponds to the absence of the O_2^- radical-anion from oxyhaemoprotein molecules. Naturally, this view in no way predetermines the solution of the problem of the amount of ionic character of the $Fe-O_2$ bond as well as the possibility or impossibility of the dissociation of the adducts $[FeO_2]^{2+}$ into Fe^{3+} and the SORA or the transition of the $Fe^{3+}O_2^-$ ion pair to the triplet state.

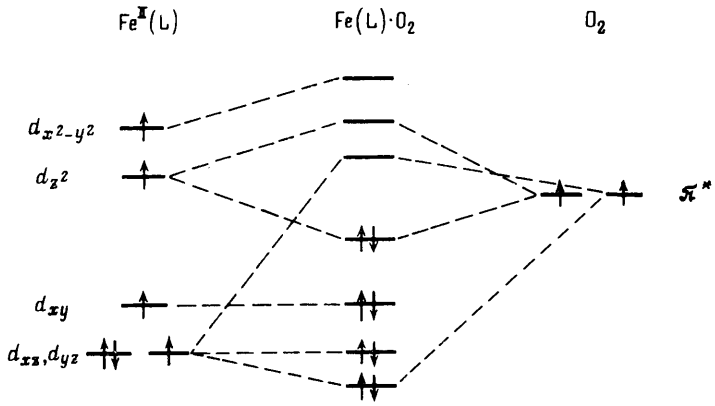


Figure 1. A molecular-orbital model of the coordination of oxygen to iron(II) complexes (L = ligand).

Recently the problem of the nature of the bond between oxygen and the metal atom in the oxygen complexes of transition metals has been vigorously discussed also in relation to octahedral oxygen complexes of bivalent cobalt. X-Ray diffraction data have shown that the oxygen atoms in the oxygen adducts of 1 : 1 cobalt(II) complexes are not equivalent and that the O–O bond length is in many instances close to that observed for the superoxide ion in KO_2.[154–156] The authors of these studies therefore regard these complexes as compounds containing tervalent cobalt and the SORA $\left[-\overset{\diagdown\ \diagup}{Co^{3+}}\cdot O_2^- \right]$.

The results of a study of the oxygen complexes of cobalt by X-ray electronic spectroscopy also agree much better with the formula $Co^{3+}\cdot O_2^-$ than with $Co^{2+}\cdot O_2$.[157,158]

The formula $Co^{3+}\cdot O_2^-$ for the oxygen complexes of cobalt was also adopted by investigators[159,160] who studied such complexes by EPR as well as investigators[161,162] who carried out quantum-mechanical *ab initio* calculations on the oxygen complexes of cobalt by the LCAO-MO-SCF method.

However, Tovrog et al.[146] published very recently a study where it is stated (these views are shared also by the authors of the present review) that the treatment of the oxygen complexes of cobalt(II) as $Co^{3+}\cdot O_2^-$ is only qualitatively correct, since the real degree of electron transfer is usually less than unity and varies in the range 0.1–0.8.

The formation of a complex between cobalt(II) compounds and oxygen has been regarded[146,162] as a result of the pairing of the spin of the electron in the d_z orbital of Co^{2+} with the spin of the electron in the π^* orbital of the oxygen atom. Depending on the strength of the ligand field around the cobalt atom, the complex approaches more or less closely the limiting case described by the formula $Co^{3+}\cdot O_2^-$.[146] The mixing of the Co^{2+} and O_2 orbitals can be represented by the diagram in Fig. 2: we have $Co^{3+}\cdot O_2^-$ for $\alpha = 0$ and $Co^{2+}\cdot O_2$ for $\alpha = \beta$.

Analogous problems concerning the nature of the metal–oxygen bond arise also for the oxygen complexes of Cu^+, Cr^{2+}, Ir^+, Ni^0, Pt^0, Pd^0, etc. For example, the ease of oxidation of copper(I) compounds has been explained by the formation of a π-complex, which is subsequently converted into a copper derivative of the SORA:[163]

$$Cu^+ + O_2 \rightleftarrows [Cu^+ \rightarrow O_2] \rightleftarrows Cu^{2+}\cdot O_2^- .$$

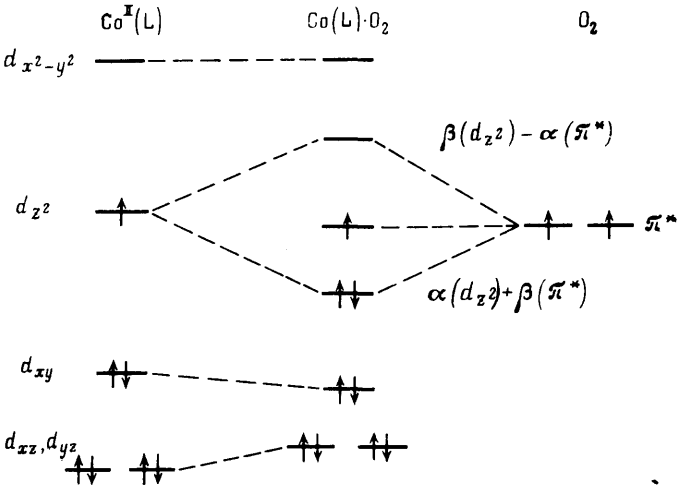


Figure 2. A molecular-orbital model of the coordination of oxygen to cobalt(II) complexes.

In the complexes $Ir(Hal)(CO)(PPh_3)_2.O_2$ the length of the O–O bond varies markedly depending on the nature of the halogen[164,165]: for Hal = Cl, it amounts to 1.30 ± 0.03 Å, while for Hal = I it is 1.47 ± 0.02 Å. Accordingly, La Placa and Ibers[164] regard these complexes as $Ir^{2+}(Cl)(CO)(PPh_3)_2\cdot O_2^-$ and $Ir^{3+}(I)(CO)(PPh_3)_2\cdot O_2^{2-}$. As a result of the difference between the structures of these complexes, reversible binding of oxygen is possible only for the complex $Ir(Cl)(CO)(PPh_3)_2$.[165]

In considering the problem of the way in which oxygen complexes of metals can serve as sources of the SORA, we shall point out the following pathways which are possible in principle:

(1) Direct dissociation (ionisation) of the complex:

$$M^{n+} + O_2 \rightleftarrows [MO_2]^{n+} \rightleftarrows M^{(n+1)+} + O_2^- .$$

On the basis of kinetic data, it is stated[166] that the oxygen complex of Cu^+ in an aqueous acetonitrile medium is capable of dissociating via the above mechanism, but the dissociation with formation of oxygen takes place at a rate which is higher by a factor of approximately 26 than the dissociation with formation of the O_2^- radical-ion.

(2) In protic media there is a possibility of indirect formation of the SORA:[34,166,167]

$$[MO_2]^{n+} + H^+ \rightarrow [MOOH]^{(n+1)+} \rightleftarrows M^{(n+1)+} + HO_2^\cdot ;$$
$$HO_2^\cdot \rightleftarrows H^+ + O_2^- .$$

In this case the formation of $HO_2^\cdot$ is significantly facilitated by the presence of anions capable of forming stable complexes with $M^{(n+1)+}$. Accordingly, the Fe^{2+}–pyrophosphate-anion–O_2 system is greatly superior, as regards the efficiency of the generation of the SORA in aqueous solution, to the analogous systems containing, instead of pyrophosphate, anions which are weaker complex-forming agents in relation to Fe^{3+}.[168]

Few data are as yet available concerning reactions of dioxygen transition metal complexes. Their study is complicated by different oxidation-reduction reactions of the substrate and its oxidation products, for example:

$$M^{(n+1)+} + RH \rightarrow M^{n+} + R^\cdot + H^+ ;$$
$$M^{(n+1)+} + ROOH \rightarrow M^{n+} + ROO^\cdot + H^+ ;$$
$$M^{n+} + ROOH \rightarrow M^{(n+1)+} + RO^\cdot + OH^- .$$

However, it has been established that the formation of complexes between oxygen and transition metal compounds alters significantly the reactivity of oxygen[140,142].

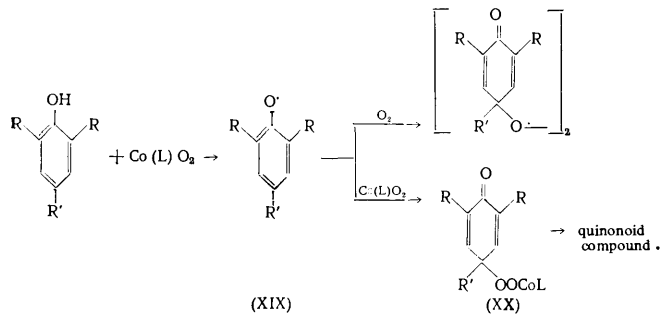
Presumably oxygen complexes of transition metal compounds containing the superoxide-like dioxygen ligand should be capable of abstracting hydrogen atoms from fairly reactive organic compounds. Indeed the available literature data confirm this view[169–173]. For example, in a study of the kinetics of the oxidation of cumene by oxygen, catalysed by the *o*-phenanthroline complex of copper, it was possible to show that the reaction of the oxygen complex of copper with cumene plays an important role in this process[171]:

$$\underset{\text{(XVII)}}{[Cu(phen)]^+} + O_2 \rightleftarrows \underset{\text{(XVIII)}}{[Cu(phen)]^{2+}\cdot O_2^-} ;$$
$$\text{(XVIII)} + RH \rightarrow \text{(XVII)} + HO_2^\cdot + R_2^\cdot ;$$
$$R^\cdot + O_2 \rightarrow RO_2^\cdot ;$$
$$RO_2^\cdot + RH \rightarrow ROOH + R^\cdot, \text{ etc.}$$

R = $PhCMe_2$; phen = *o*-phenanthroline.

It is appropriate to mention here that the abstraction of a hydrogen atom from cumene takes place also under the influence of alkali metal superoxides[31]. The oxidising properties of O_2 complexes with cobalt(II) compounds have been demonstrated convincingly also in relation to the complex $[Co(3\text{-MeO-Salen})\cdot O_2]^{2+}$.[174] This complex readily oxidises thiols, ascorbic acid, hydroquinone, and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine. In the last two instances it was shown by EPR that semiquinone radicals and the *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine radical-cation are formed respectively.

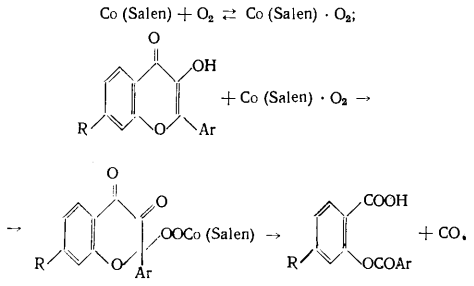
It has been demonstrated that cobalt complexes capable of reversible binding of oxygen behave as homogeneous catalysts of the oxidation of substituted phenols by oxygen under mild conditions, which leads to a mixture of various quinonoid compounds[175-177].



(XIX) (XX)

Complex (XX), where R = R′ = t-C_4H_9 and L = bis-(3-salicylideneaminopropyl)amine dianion, was isolated in the reaction of 2,4,6-tri-t-butylphenol with a stoichiometric amount of CoL and oxygen[177]. Compound (XX) is also formed as a result of the recombination of two radicals—(XIX) and $Co(L)O_2$.

The *N,N′*-bis(salicylidene)ethyleneaminate complex of cobalt(II) [Co(Salen)], which is an effective oxygen transferring agent, catalyses at room temperature the oxidation of hydroxyflavones, simulating the enzymic oxidation of quercetin[178]:



It is of interest to note that the ability of various metal compounds having reducing properties to activate molecular oxygen by its partial reduction is apparently not unique. It appears almost self-evident that, in principle, there should exist activators of molecular oxygen which do not contain reducing metals at all. Thus, in the oxidation of cumene with oxygen, magnesium-phthalocyanine exhibits a catalytic activity[179]:

$$Pc + O_2 \rightleftarrows Pc \cdots O_2 \rightleftarrows Pc^{+} \cdots O_2^{-} \quad (XXI)$$

$$RH + (XXI) \rightarrow Pc + R^{\cdot} + HO_2^{\cdot};$$

R = $PhCMe_2$; Pc = magnesium-phthalocyanine.

The ability of the substrate to form complexes with oxygen clearly depends not only on the nature of the metal but also on the nature of its ligand environment and is thus a general property of the enzyme-like molecule. The study of metal complexes with ligands capable of undergoing ready and reversible one-electron transitions, which only partly involve the valence shell of the metal, is therefore particularly promising. Complexes with paramagnetic ligands are of special interest at the present time.

6. The Role of the SORA in Biochemical Processes

The study of the role of the SORA in living systems was stimulated by the studies of McCord and Fridovich[29,180-182] carried out in 1968–1970. Subsequent investigations initiated a new field in biochemistry—the biochemistry of the SORA. It became clear that the SORA plays an important role in all aerobic cells.

Molecular oxygen plays the role of a readily available electron acceptor in various biochemical oxidation reactions. As a result of such processes, the electrons of the oxidised substrates are passed to the electron transferring enzymes and then further to oxygen molecules, which are converted into the SORA.

The high reactivity of the SORA and of the hydroperoxy-radical, which always accompanies it in aqueous solutions, as well as the possibility of the formation of hydroxy-radicals in systems of this kind are responsible for the toxic effect of the SORA on living tissues[29,183-188]. In 1969 McCord and Fridovich discovered the first example of enzymes which protect living systems from the toxic activity of the SORA by its catalytic disproportionation[29]:

$$O_2^{\cdot-} + 2H^{+} \xrightarrow{\text{enzyme}} H_2O_2 + O_2;$$

$$H_2O_2 \xrightarrow{\text{catalase}} H_2O + O_2.$$

This enzyme proved to be the copper-containing protein erythrocuprein, which had been known already for more than thirty years[189]. Other proteins, fulfilling an analogous function and given the general name of superoxide dismutases (SOD), were discovered subsequently. The active centres of the SOD are usually copper atoms: certain simple copper compounds also possess superoxide dismutase properties[190,191]. However, SOD containing metals other than copper are also known[192,193]. Vigorous research in recent years established the presence of SOD in living objects such as human cells[189,194,195], animal livers[196], plant leaves[179,198], wheat grains[199], and rod cells in animal eyes[200], yeasts[193,201], guinea pig leucocytes[202], etc.

The following sequence of reactions has now been adopted as the mechanism of the enzymic disproportionation of the SORA:[203,204]

$$E + O_2^{-} \rightarrow E^{-} + O_2 \quad (k = 1.2 \pm 0.2 \cdot 10^9 \text{ litre mole}^{-1} \text{ s}^{-1});$$

$$E^{-} + O_2^{-} \xrightarrow{2H^{+}} E + H_2O_2 \quad (k = 1 - 3 \cdot 10^9 \text{ litre mole}^{-1} \text{ s}^{-1});$$

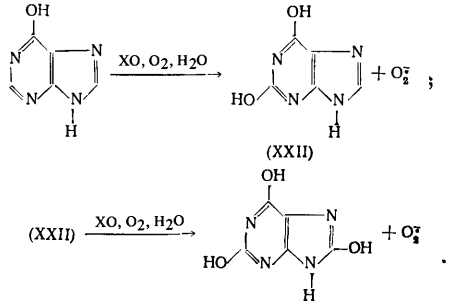
$$E^{2-} + O_2^{-} \xrightarrow{2H^{+}} E^{-} + H_2O_2 \quad (k = 1.2 \pm 0.2 \cdot 10^9 \text{ litre mole}^{-1} \text{ s}^{-1});$$

E = erythrocuprein.

It is extremely significant that, in contrast to spontaneous dissociation, enzymic dissociation does not lead to the formation of toxic singlet oxygen[188].

Following the discovery of the superoxide dismutase properties of erythrocuprein and other proteins, biochemists and organic chemists acquired a valuable test, which makes it possible to confirm or disprove the involvement of the SORA in a particular process. The system believed to generate the SORA is usually treated with compounds capable of reacting with the SORA; these are normally ferricytochrome *c* [29] and Nitrotetrazolium Blue,[53,183] which are reduced by the SORA to ferrocytochrome *c* ($k = 1.4 \times 10^6$ litre $mole^{-1}$ s^{-1};[205] $HO_2^{\cdot}$ does not reduce ferricytochrome *c* [205]) and formazan respectively, as well as adrenalin, which is oxidised by the SORA to adrenochrome[85]. If the system does indeed induce any of these reactions and catalytic amounts of SOD inhibit it fully (or significantly), it is concluded that the SORA is formed in the given system.

The formation of the SORA has been established in many enzymic and non-enzymic systems. The enzymic system which has been most thoroughly investigated and most frequently used for the generation of the SORA consists of a mixture of xanthine with a catalytic amount of xanthine oxidase (XO), which converts xanthine into uric acid in the presence of oxygen[32,180,181,206]. Hypoxanthine can be used instead of xanthine[185]:

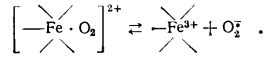


(XXII)

It is believed that oxygen is reduced to the SORA by the reduced form of the isoalloxazine ring of the flavin-adenine dinucleotide associated with xanthine oxidase[207,208].

Oxygen is also reduced to the SORA when it is treated by the reduced form of a simpler flavin compound—flavin mononucleotide[182,208,209]. The formation of the SORA in the reaction of reduced flavins with oxygen was demonstrated directly by EPR.[210]

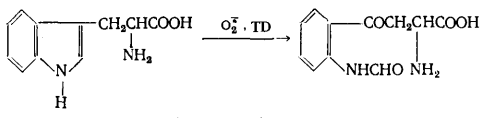
Misra and Fridovich[211], who discussed the problem of the possible generation of the SORA from the oxygen complexes of haemoproteins, noted that even their simple dissociation might lead to the SORA:



The properties of the SORA suggest the possibility of its formation from oxyhaemoglobin. Thus, in contrast to haemoglobin and methaemoglobin, the denaturation of oxyhaemoglobin by heat is accompanied by oxidation of its sulphydryl groups[212]. Catechol, hydroquinone[213], and aniline[214] exhibit a catalytic effect on the $HbFe.O_2 \rightarrow$ MetHbFe transition (as already mentioned, polyhydric phenols are capable of binding the SORA).

It has been possible to show that the autoxidation of haemoglobin in the presence of adrenalin leads to the oxidation of the latter to adrenochrome, which is inhibited by the addition of SOD.[211] These data indicate the formation of the SORA from oxyhaemoglobin. Other haemoproteins are also capable of generating the SORA from oxygen. Thus it has been concluded that the SORA is formed by the autoxidation of certain cytochromes[215,216].

The involvement of the SORA in the cleavage of tryptophan to formylkynurenine, catalysed by tryptophan 2,3-dioxygenase (TD), has also been demonstrated[217]:



The reaction is inhibited by SOD and the addition of electrochemically generated Bu_4NO_2 to a mixture of tryptophan and the enzyme leads to the rapid formation of formylkynurenine in an amount proportional to that of the added Bu_4NO_2.[217]

Horseradish peroxidase is also capable of reducing oxygen to the SORA.[218] The generation of the SORA by proteins containing non-haem iron (ferredoxins) has been demonstrated both with the aid of SOD[219] and by the direct detection of SORA with the aid of EPR.[206,220] Copper proteins are apparently likewise capable of generating the SORA from oxygen in certain instances[221].

It is extremely significant that photosynthesis is also accompanied by the generation of the SORA.[222-226] It is believed that it is formed on reduction of oxygen with ferredoxins and is consumed in the dehydrogenation of ascorbic acid. The familiar Hill reaction[227], which involves methylviologen as an electron acceptor, similarly leads to the formation of the SORA as a result of the reduction of oxygen by the methylviologen radical-cation[94,228].

The involvement of the SORA in the autoxidation of phenylhydrazine[229], mercaptans[112], and polyhydric phenols[87,230] and in the reaction of oxygen with the reduced form of phenazinium methosulphate has also been demonstrated with the aid of SOD.[231]

Phenothiazine derivatives, whose metabolism in the organism reduces to their conversion into S-oxides, give rise to S-oxides also on treatment with the SORA, which may indicate the involvement of the latter in the metabolism of medicinal substances derived from phenothiazine[232].

The enzymic reduction of nitro-compounds, which proceeds via the formation of their radical-anions, is inhibited by oxygen apparently in consequence of the reaction[233]

$$RNO_2^{\cdot-} + O_2 \rightarrow RNO_2 + O_2^{\cdot-} .$$

The inhibiting effect of SOD has been observed in the study of its influence on hydroxylation by a number of model non-enzymic systems[234,235]. SOD acts similarly also on a number of enzymic hydroxylation processes[236-239]. One can therefore assume that hydroxylation is in such cases a SORA-dependent process. However, the fact that the inhibition of hydroxylation by SOD is not complete may indicate the simultaneous operation of other, SORA-independent hydroxylation mechanisms. In addition to all other species involved in this process, the hydroxylating agents can be the $HO_2^{\cdot}$ radical and the hydroxy radical generated, for example, via the mechanism[235,240]

$$O_2^{\cdot-} + H_2O_2 \rightarrow O_2 + {}^{\cdot}OH + OH^- .$$

Studies in recent years[241,242] indicated the important role of the SORA in the mechanism of the bactericidal action of human leucocytes. The phagocytosis of latex particles or *Propionibacterium Shermanii* leads to chemiluminescence[243]. The addition of SORA oxidants (Nitrotetrazolium Blue or cytochrome *c*) lowers its intensity; SOD inhibits both chemiluminescence[244] and the reduction of oxidants by SORA[243]. These findings show that the bactericidal action of leucocytes is a SORA-dependent process. However, the direct bactericidal agent is not SORA, but the singlet oxygen formed from it. This is confirmed by the greater resistance to phagocytosis of bacteria containing carotenoids [powerful $O_2(^1S)$ quenching agents] compared with the analogous bacteria which do not contain them[245]. In this case the NADPH–NADPH oxidase system (NADPH is reduced nicotinamide-adenine dinucleotide phosphate) is responsible for the generation of the SORA.

The involvement of the SORA has also been postulated in various lipid oxidation processes[123,246-248], because the latter can be inhibited by SOD. Like the bactericidal

action of leucocytes, the oxidation of lipids is apparently caused by the singlet oxygen formed in the disproportionation of the SORA.[123] This is indicated by the inhibition of the oxidation of lipids by 1,3-diphenylisobenzofuran, which is an effective acceptor of singlet oxygen[123].

III. OTHER OXYGEN RADICAL-ANIONS

1. The Radical-Anion of Atomic Oxygen (ORA)

The properties of the ORA ($O^{\cdot-}$) have been little studied hitherto, in contrast to its conjugate acid—the hydroxy-radical. However, the data already available indicate a significant difference between the properties of the ORA and the hydroxy-radical[249].

The EPR signal of $O^{\cdot-}.nH_2O$, which consists of a broad singlet line, has been observed following the ultraviolet irradiation of frozen alkaline solutions in hydrogen peroxide[250].

The usual method for the generation of the ORA involves the radiolysis of aqueous solutions of alkali saturated with nitrous oxide[251]. Nitrous oxide then behaves as an acceptor of hydrated electrons and decomposes with formation of the ORA:

$$H_2O \xrightarrow{\gamma} H^{\cdot} + {}^{\cdot}OH + e^-_{aq} + H^+ \ ;$$
$${}^{\cdot}OH + OH^- \rightarrow O^{\cdot-} + H_2O \ ;$$
$$N_2O + e^-_{aq} \rightarrow N_2O^{\cdot-} \rightarrow N_2 + O^{\cdot-} \ .$$

Nitrous oxide can be replaced by ammonium persulphate[252]:

$$S_2O_8^{2-} + e^-_{aq} \rightarrow SO_4^{3-} + SO_4^{\cdot-} \ ;$$
$$SO_4^{\cdot-} + 2OH^- \rightarrow SO_4^{2-} + O^{\cdot-} + H_2O \ .$$

The rate of reaction of the hydroxy-radical with potassium hexacyanoferrate(III) falls markedly with increase of the pH of the medium, which has been interpreted as a result of the dissociation of the hydroxy-radical, leading to the less active ORA:[253,254]

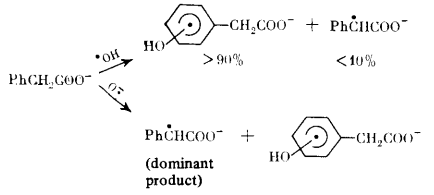
$${}^{\cdot}OH \rightleftarrows O^{\cdot-} + H^+ \ ;$$
$$Fe(CN)_6^{4-} \xrightarrow{{}^{\cdot}OH(O^{\cdot-})} Fe(CN)_6^{3-} \ ;$$
$$pK = 11{,}9 \ .$$

The main pathway in the destruction of the ORA in aqueous solution involves recombination to the peroxide ion[253]:

$$O^{\cdot-} + O^{\cdot-} \rightarrow O_2^{2-} \quad (2k = 2 \cdot 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}).$$

Kinetic parameters have now been obtained for a number of reactions in which the ORA behaves as an electron or hydrogen atom acceptor. The rate constants for the one-electron oxidation of the Br^-, I^-, SCN^-, Fe^{2+}, $Fe(CN)_6^{4-}$, and $C_6H_5O^-$ ions as well as aniline by the radical-anion $O^{\cdot-}$ are in the range $(0.03-3)\times 10^9$ litre mole^{-1} s^{-1}. Reactions involving the abstraction of hydrogen atoms from a number of organic substrates (CH_3OH, CH_3CN, polymethylbenzenes, pyrrolidine) are characterised by rate constants in the range $(0.22-21)\times 10^9$ litre mole^{-1} s^{-1}.[257-260]

Comparison of the reactivities of the ORA and the hydroxy-radical in reactions with organic compounds shows that the ORA is usually less reactive than the conjugate acid. At the same time, in reactions involving the abstraction of atomic hydrogen from organic compounds the reactivity of the ORA is only slightly inferior to that of the $^{\cdot}OH$ radical, but the rates of addition of the ORA to aromatic systems are smaller by 2–3 orders of magnitude than in the case of the hydroxy-radical. This leads to a significant change of the relative rates of the competing processes on passing from acidic and weakly alkaline media to strongly alkaline media. Thus, whereas at pH values corresponding to acidic and weakly alkaline media the dominant pathway in the reactions with many aromatic derivatives is addition of the hydroxy-radical to the aromatic ring, on passing to high pH values the abstraction by atomic oxygen radical-anions of hydrogen atoms which are not linked directly to the aromatic ring predominates[259,261,262].



Using an ionic cyclotron resonance mass-spectrometer, a study has been made of the reactions of the ORA with unsaturated hydrocarbons involving the abstraction of a proton:

$$CH{\equiv}CH + O^{\cdot-} \rightarrow C_2H^- + {}^{\cdot}OH \ ;$$
$$MeCH{=}CH_2 + O^{\cdot-} \rightarrow C_3H_5^- + {}^{\cdot}OH \ .$$

which can sometimes be accompanied by the subsequent abstraction of a hydrogen atom:

$$CH_2{=}CH_2 + O^{\cdot-} \rightarrow C_2H_3^- + H_2O \ ;$$
$$CH_2{=}CF_2 + O^{\cdot-} \rightarrow CF_2C^{\cdot-} + H_2O$$

which formally corresponds to the abstraction of the H_2^+ radical-cation from the substrate[263].

The oxidation of acetone by hydroxy-radicals and the ORA leads to different products[264]:

$$Me_2CO + {}^{\cdot}OH \rightarrow MeCOCH_2^{\cdot} \xrightarrow{O_2,\,H_2O} \rightarrow MeCOCOOH \ ;$$
$$Me_2CO + O^{\cdot-} \rightarrow Me{-}\underset{\displaystyle {}^{\cdot}O\quad O^-}{\overset{\displaystyle |\quad |}{C}}{-}Me \rightarrow MeCOO^- + Me^{\cdot} \ ;$$
$$Me^{\cdot} \dashrightarrow \rightarrow CH_2O \ .$$

2. The Ozone Radical-Anion (OzRA)

The ozone molecule exhibits a very high electron affinity (2.14 ± 0.15 eV,[265] 2.09 eV[266]), readily combines with an electron, and is converted into the OzRA ($O_3^{\cdot-}$). The OzRA salts of alkali metals (Na, K, Ru, Cs) and the $N(CH_3)_4^+$ cation[267-269] have been isolated in a pure state. They are usually obtained by treating solid alkalis[267,268] or alkali metal superoxides[270-272] with ozonised oxygen:

$$O_3 + MOH \rightarrow M^+O_3^{\cdot-} + {}^{\cdot}OH \ ;$$
$${}^{\cdot}OH + MOH \rightarrow M^+O^{\cdot-} + H_2O, \quad M = Na, K, Rb, Cs, \text{ or } NMe_4 \ ;$$
$$M^+O^{\cdot-} + O_3 \rightarrow M^+O_3^{\cdot-} + O_2 \ ;$$
$$M^+O_2^{\cdot-} + O_3 \rightarrow M^+O_3^{\cdot-} + O_2 \ .$$

Alkaline earth metal ozonides, which are stable only at low temperatures, can be obtained by the ozonisation of the peroxides of these metals[273,274].

Aqueous solutions of alkali containing nitrous oxide and oxygen are used to generate the OzRA in studies by pulse radiolysis[275-277]:

$$H_2O \xrightarrow{\gamma,\,N_2O,\,OH^-} O^{\cdot-} \ ;$$
$$O^{\cdot-} + O_2 \rightarrow O_3^{\cdot-} \quad (k = 2.5 \cdot 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}) \text{ (Ref.275).}$$

Alkali metal ozonides are orange or red crystalline compounds whose lattice is made up of regularly alternating alkali metal ions and O_3^- species. It has been found that[278] the O–O bond length in the O_3^- radical-anion is 1.19 Å and the O–O–O angle is 100°.†

Alkali metal ozonides dissolve in liquid ammonia, forming paramagnetic solutions. The maximum of the O_3^- absorption band is near 450 nm (liquid ammonia)[269,280] and in the region of 430–438 nm (water)[275–277].

The OzRA salts are rapidly decomposed by water via the mechanism[281]

$$MO_3 + H_2O \rightarrow {}^{\cdot}OH + O_2 + MOH\,.$$

It has been noted that this reaction can serve as a powerful source of hydroxy-radicals, which are formed in the absence of metal cations capable of forming complexes with them[282].

Low temperatures and a highly alkaline medium increase the stability of the OzRA in an aqueous medium (the half-life in 8 M KOH at −50 °C is 12 min)[43].

Virtually nothing is known about the organic reactions of alkali metal ozonides. It has been noted that solid KO_3 is capable of initiating the chain oxidation of acetaldehyde by oxygen, which is distinguished by an unusual chain length (more than 10^4 CH_3CHO molecules react per KO_3 molecule)[283]. The mechanism of the reactions of ozone with organic compounds has been comparatively little studied[284]. The initial stage in the oxidation of saturated hydrocarbons RH by ozone is a simple bimolecular reaction[285,286]. The most probable products under these conditions are the R˙ and ˙OH radicals and oxygen[287–291]. Like the oxidation of hydrocarbons by oxygen, their reaction with ozone apparently includes an electron transfer stage, which precedes the formation of weak CTC:[292–294]

$$RH + O_3 \rightleftarrows RH \ldots O_3 \rightleftarrows [RH^{+\cdot} \ldots O_3^-] \rightarrow [R^{\cdot} + O_2 + {}^{\cdot}OH] \begin{cases} \longrightarrow ROH + O_2 \\ \longrightarrow R^{\cdot} + O_2 + {}^{\cdot}OH. \end{cases}$$

Whereas in the reaction with oxygen the abstraction of a hydrogen atom by a triplet oxygen molecule can serve as an alternative mechanism, such an explanation is altogether impossible for the diamagnetic ozone.

At low temperatures, where the thermal oxidation reaction does not occur, the irradiation of ozone solutions in saturated hydrocarbons leads to their photochemical oxidation[294]. This apparently entails a photoinduced electron transfer to the CTC. Analysis of the composition and ratio of the oxidation products (alcohols, ketones) indicates the similarity of the mechanisms of the photochemical and thermal reactions of ozone with saturated hydrocarbons. In addition, both reactions of ozone with isomeric decalins proceed with approximately the same degree of retention of the configuration of the oxidation products[294].

The first stage in the oxidation with ozone of various organometallic compounds[108] as well as organic compounds containing heteroatoms[284] (amines, sulphides, nitroxy-radicals) also involves the formation of the OzRA as a result of electron transfer from the substrate to ozone.

The oxidation of trimesitylvinyl alcohol to the radical (XXIII) under the influence of ozone has been described[295]:

$$Mes_2C{=}C(OH)\,Mes + O_3 \rightleftarrows Mes_2C{=}C(OH)\,Mes \ldots O_3 \rightarrow \rightarrow \left[\left(\begin{array}{c} OH \\ | \\ Mes_2C{=}CMes \end{array}\right)^{\ddagger} \ldots O_3^-\right] \rightarrow Mes_2\dot{C}COMes\,.$$

(XXIII)

† In free ozone the O–O bond length is 1.26 Å and the O–O–O angle is 127°.[279]

The epoxidation of olefins and aromatic compounds by ozone begins in the same way:

$$\begin{array}{c} \diagup\!\!\diagdown C{=}C \diagup\!\!\diagdown + O_3 \rightleftarrows \diagup\!\!\diagdown C{=}C \diagup\!\!\diagdown \ldots O_3 \rightleftarrows \left[\left(\diagup\!\!\diagdown C{-}C \diagup\!\!\diagdown\right)^{\ddagger} \ldots O_3^-\right] \rightarrow \\ \rightarrow \left[\left(\diagup\!\!\diagdown C{=}C \diagup\!\!\diagdown\right)^{\ddagger} \ldots O^- \ldots O_2\right] \rightarrow -C\overset{O}{\diagup\!\!\diagdown}C- + O_2\,. \end{array}$$

In fact, as already mentioned, the OzRA is capable of dissociating into the ORA and O_2 ($k = 3.3 \pm 0.3 \times 10^3$ s^{-1}; 25 °C).[257]

In aqueous solutions of alkali, ozone decomposes via the mechanism[296]

$$\begin{gathered} O_3 + OH^- \rightarrow O_3^- + {}^{\cdot}OH\,; \\ {}^{\cdot}OH + OH^- \rightarrow O^{-\cdot} + H_2O\,; \\ 2O^{-\cdot} + H_2O \rightarrow O + 2OH^-\,; \\ O^{-\cdot} + O \rightarrow O_2^-\,; \\ 2O_3^- + H_2O \rightarrow HO_2^- + OH^- + O_2\,. \end{gathered}$$

The formation of the ˙OH radicals and the ORA is responsible for the extremely effective oxidising properties of ozone in an alkaline medium in relation to organic compounds (the final oxidation products are CO_2 and H_2O).[297] In the $O_3^- \rightleftharpoons O_2 + O^-$ system the most active species is the ORA, so that many reactions of the OzRA are in fact reactions of the ORA.

IV. THE CARBON DIOXIDE RADICAL-ANION

The existence of the carbon dioxide radical-anion (CRA) CO_2^- was demonstrated at the beginning of the 1960s in a study of the EPR spectra of alkali metal formate crystals subjected to γ- or X-irradiation[298–300].

In contrast to the carbon dioxide molecule, the CRA is non-linear[299,301]; the O–C–O angle is approximately 135°. The EPR spectrum of the CRA in aqueous solution (singlet line with $g = 2.0040$) has been observed in two investigations[104,302]. The available data concerning the magnitude of pK for the equilibrium $^{\cdot}COOH \rightleftharpoons CO_2^- + H^+$ are contradictory: 2.8 (Gutlbauer and Getoff[303]) and 1.4 (Buxton and Sellers[304]).

Since the CO_2 molecule apparently has a negative electron affinity (−0.36 eV according to the results of a quantum-mechanical calculation[301]) its direct chemical reduction proceeds with difficulty and is not at present used to generate the CRA. The simplest method of generating the CRA in an aqueous medium involves the interaction of hydroxy-radicals with formates. Hydrogen peroxide is usually reduced by Ti^{3+} salts in the presence of formate ions[104,305]:

$$\begin{gathered} Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + {}^{\cdot}OH + OH^-\,; \\ {}^{\cdot}OH + HCO_3^- \rightarrow CO_2^- + H_2O \\ (k = 2.7 \cdot 10^9 \text{ litre mole}^{-1}\,s^{-1}). \end{gathered}$$

The CRA is unstable and is rapidly converted into formate, bicarbonate, and oxalate anions and carbon monoxide[306–309]. The formation of the formate anion under these conditions undoubtedly begins with the protonation of the CRA. The subsequent stages may involve the reduction of the carboxy-radical and the protonation of the resulting formate anion. It has been suggested that the carbonate ion and carbon monoxide can be formed via a bimolecular reaction[306,309], but the possibility of the

unimolecular fragmentation of the CRA cannot be ruled out either:

$$CO_2^{\cdot-} + H_2O \rightleftarrows {}^{\cdot}COOH + OH^-;$$
$$^{\cdot}COOH + CO_2 \xrightarrow{-CO_2} {}^{-}COOH;$$
$$^{-}COOH \begin{cases} \longrightarrow HCOO^- \\ \xrightarrow{H^+} HCOOH \end{cases};$$
$$2CO_2^{\cdot-} \rightarrow CO_3^{2-} + CO;$$
$$CO_3^{2-} + H^+ \rightarrow HCO_3^-;$$
$$2CO_2^{\cdot-} \rightarrow (-COO^-)_2.$$

The electrochemical reduction of carbon dioxide in dimethyl sulphoxide, which takes place at high cathodic potentials (−1.9 to −2.0 V) according to coulometric measurements, may consist in the transfer of one electron (gold cathode) or between one and two electrons (mercury cathode) to the CO_2 molecule[306]. The main products are carbon monoxide and the bicarbonate anion.

The CRA is also formed when hydrated electrons, generated in the radiolysis of water, are accepted by carbon dioxide[310]:

$$CO_2 + e_{aq}^- \rightarrow CO_2^{\cdot-} \quad (k = 7.7 \cdot 10^9 \text{ litre mole}^{-1}\text{ s}^{-1}).$$

In this case the formation of the CRA is demonstrated, in particular, by the fact that in the presence of aliphatic alcohols they are carboxylated to α-hydroxyacids[311]:

$$H_2O \xrightarrow{\gamma} H^{\cdot} + {}^{\cdot}OH + e_{aq}^- + H^+;$$
$$e_{aq}^- + CO_2 \rightarrow CO_2^{\cdot-};$$
$$RCH_2OH + {}^{\cdot}OH \xrightarrow{-H_2O} R\dot{C}HOH;$$
$$R\dot{C}HOH + CO_2^{\cdot-} \rightarrow RCH(OH)COO^-.$$

The CRA can also be generated by the one-electron oxidation of the oxalate anion. Examples of such reactions known at the present time are associated with the decomposition of tervalent manganese[312] and cobalt[313] oxalates and the chain oxidation of oxalate anions by persulphates[314]:

$$[M(C_2O_4)_n]^{(3n-3)-} \rightarrow M^{2+} + (n-1)C_2O_4^{2-} + CO_2^{\cdot-} + CO_2;$$
$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\cdot-};$$
$$SO_4^{\cdot-} + C_2O_4^{2-} \rightarrow SO_4^{2-} + CO_2^{\cdot-} + CO_2;$$
$$CO_2^{\cdot-} + S_2O_8^{2-} \rightarrow CO_2 + SO_4^{\cdot-} + SO_4^{2-} \text{ etc.}$$

Reactions in which the CRA behaves as a one-electron reductant are most characteristic of this radical-anion. Thus, when a solution of manganese(III) oxalate is decomposed thermally in the presence of oxygen, an appreciable amount of H_2O_2 is formed[312], apparently from superoxide radical-anions:

$$CO_2^{\cdot-} + O_2 \rightarrow CO_2 + O_2^{\cdot-} \quad (k = 4.6 \cdot 10^9 \text{ litre mole}^{-1}\text{ s}^{-1}) \text{ (Ref.315)}.$$
$$2O_2^{\cdot-} + H_2O \rightarrow H_2O_2 + O_2.$$

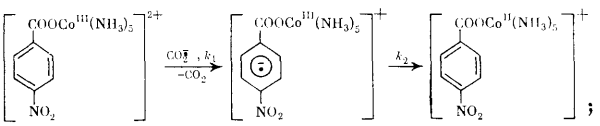
The interaction of the CRA with alkyl halides[316,317] and also with compounds having an N–halogen bond[318] leads to the dissociative capture of an electron by halide molecules; the free radicals formed in this process have been identified by EPR:[317,318]

$$RX + CO_2^{\cdot-} \rightarrow R^{\cdot} + X^- + CO_2;$$
$$MeCONHBr + CO_2^{\cdot-} \rightarrow MeCONH^{\cdot} + Br^- + CO_2.$$

Apparently all iodo-derivatives as well as sufficiently reactive bromides and chlorides react with the CRA.[317]

The ability of the CRA to transfer an electron to the *p*-nitrophenyl diazonium cation[319], quinones[315,320], aliphatic nitro-compounds[319], nitrobenzene[321], acetaldehyde, acetone and certain other carbonyl compounds[322], maleimide[323], riboflavin[324], and a number of dyes[325] has been demonstrated.

Under the influence of the CRA, the complexes of tervalent cobalt and ruthenium are reduced to the corresponding derivatives of the bivalent metals[326–328]. The reduction of the CRA by *p*-nitrobenzoatopentammine-cobalt(III) ion is of particular interest[328]. In this case it was possible to detect by ultraviolet spectroscopy the primary reduction product [the radical-ion (XXIV)], which is converted by an intramolecular electron transfer into the final product—the *p*-nitrobenzoatopentammine-cobalt(II) complex:



(XXIV)

$k_1 = 4.9 \cdot 10^9$ litre mole^{-1} s^{-1}; $k_2 = 2.6 \cdot 10^3$ s^{-1}.

Certain reactions are known[319] which can be classified as free-radical additions of the CRA to multiple bonds (demonstrated with the aid of EPR):

$$RCH{=}\overset{+}{N}(O^-)O^{\cdot} + CO_2^{\cdot-} \rightarrow \underset{\displaystyle CO_2^-}{\overset{\displaystyle |}{RCH}}{-}N(O^-)O^{\cdot};$$
$$R^1R^2C{=}NOH + CO_2^{\cdot-} \rightarrow R^1R^2C(CO_2^-)NHO^{\cdot}.$$

In connection with the recent hypothesis of the possible involvement of the CRA in photosynthetic processes[7], the following considerations may be noted.

(1) The reduction to the CRA constitutes an extremely effective means of activating carbon dioxide.

(2) Since the fixation of carbon dioxide is a dark process, the problem arises of the nature of the reductant capable of reducing CO_2 molecules, which are fairly difficult to reduce. In this connection, one can postulate the possibility of the reduction of carbon dioxide to the CRA even by comparatively weak reductants when the molecules of the latter and CO_2 are located in different parts of the homogeneous systems at whose boundary the electrical double layer is capable of exerting a catalytic effect on electron transfer to CO_2. For example, it has been stated that pyrenesulphonic acid, which is incapable of being reduced by the CRA in a homogeneous medium, is readily reduced in the solubilised state (positively charged micelles) by the CRA present in the aqueous phase[329].

The electrical double layer apparently has an analogous influence in the photochemical oxidation of water by chlorophyll in the octane–water system (under homogeneous conditions, water is not oxidised)[330].

(3) The oxalic acid present in the leaves of certain plants can be a product of the dimerisation of the CRA.

V. THE $SO_4^{\cdot-}$ RADICAL-ANION

The formation of the sulphate radical-anion (SRA) $SO_4^{\cdot-}$ was first postulated as the initial stage in oxidation by alkali metal persulphates:

$$S_2O_8^{2-} \rightleftarrows 2SO_4^{\cdot-}.$$

Subsequently this view became generally accepted. The SRA is formed fairly rapidly only on heating aqueous solutions of persulphates to 80–100°C. At lower temperatures the CRA can be conveniently generated either

photochemically[331] or by treating persulphates with reductants (Fe^{2+}, Ti^{3+}, etc.)[332,333]:

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\cdot-} ;$$

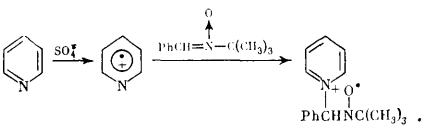
$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\cdot-} + SO_4^{2-} + M^{(n+1)+} .$$

An anisotropic EPR signal ($g_1 = 2.004$; $g_2 = 2.012$; $g_3 = 2.030$), apparently due to the SRA, was detected in a study of crystalline barium sulphate labelled with the radioactive isotope ^{35}S.[334] The EPR signal of the SRA in solution has been detected[302].

The chemical properties of the SRA show that it is a powerful one-electron oxidant. Aromatic compounds are readily oxidised by this species to radical-cations[333,335,336]:

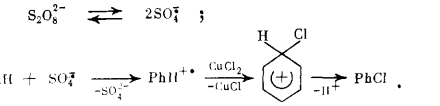
$$ArH + SO_4^{\cdot-} \rightarrow ArH^{+\cdot} + SO_4^{2-} .$$

Direct evidence for the formation of the radical-cations in the reaction of the SRA with aromatic compounds was obtained with the aid of EPR.[336] Even pyridine[337] and its derivatives[338] can be oxidised to radical-cations by treatment with the SRA. The formation of the pyridinium radical-cation was demonstrated with the aid of a spin-trapping agent (2-methyl-2-nitrosopropane)[337,338]:

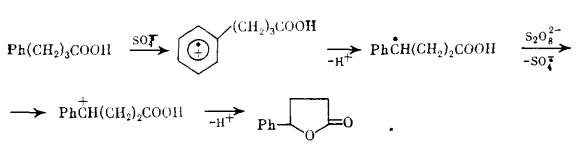


An interesting method for the chlorination of benzene and its homologues is based on the oxidation of these compounds to radical-cations; it consists in heating them with a mixture of sodium persulphate and copper(II) chloride in an aqueous acetonitrile medium[335]:

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^{\cdot-} ;$$



A convenient method has been proposed for the synthesis of the lactone of γ-hydroxy-γ-phenylbutyric acid, based on the oxidation of γ-phenylbutyric acid[339]:



The interaction of the SRA with certain saturated compounds also begins with the abstraction of an electron from the latter[79,80,340]:

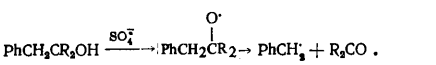
$$R^1R^2CHOH + SO_4^{\cdot-} \xrightarrow[-SO_4^{2-}]{} R^1R^2\dot{C}HOH \xrightarrow[-H^+]{} R^1R^2CHO \xrightarrow[-R^1R^2CHOH]{R^1R^2CHOH} R^1R^2\dot{C}OH$$

$$R_2S_2 + SO_4^{\cdot-} \xrightarrow[-SO_4^{2-}]{} R_2S_2^{\cdot+} .$$

Previously the reaction with alcohols was treated as abstraction of an α-hydrogen atom by the $SO_4^{\cdot-}$ radical-anion[341,342].

Alkoxy-radicals are also formed in the photochemical oxidation of alcohols by paraquat dichloride[343] and iron(III) compounds[344] as well as quinones[345].

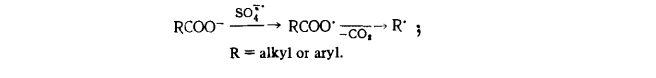
In the reaction with the SRA various alcohols, having the general formula $PhCH_2CR_2OH$, undergo oxidative fragmentation[80,333] (demonstrated by the spin-trapping method[80]):



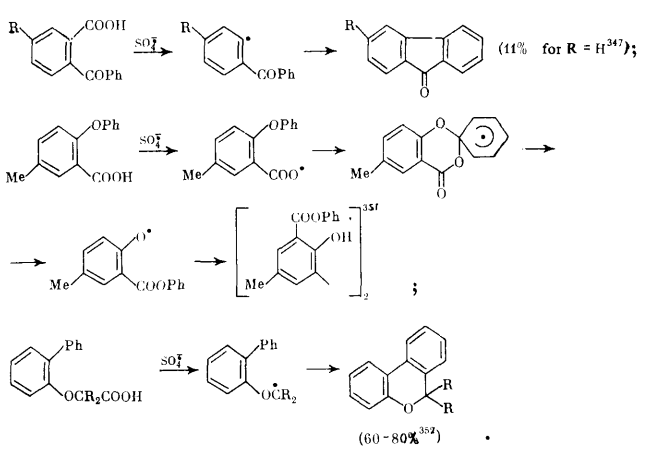
The reaction of the SRA with the nitromethane anion leads to the nitromethyl radical[346]:



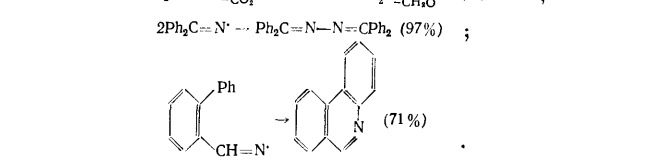
The SRA has found an important application in a simple and convenient method for the generation of alkyl and aryl radicals in aqueous solutions by the oxidative decarboxylation of carboxylic acids[333,347-350]:



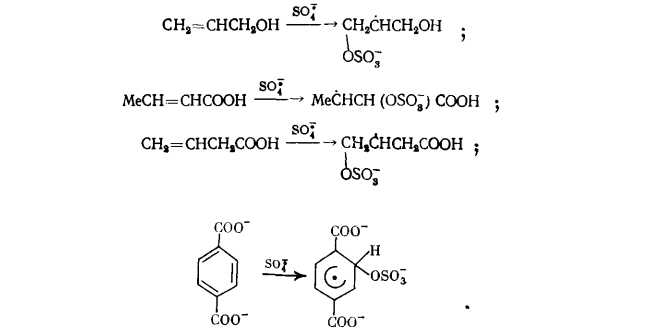
In many instances the free radicals formed in the oxidation of carboxylic acids cyclise or fragment, which can be of definite synthetic interest:



Oxidative decarboxylation under the influence of the SRA can be used for the generation of iminyl radicals[353,354]:



Apart from the reactions in which the SRA behaves as an oxidant, reactions involving the addition of the SRA to unsaturated compounds are also known[333]:



It is interesting that the EPR spectra of the adducts of the SRA with a number of unsaturated acids (for example, maleic and fumaric) can be observed only at fairly high pH, which is associated with the greater reactivity of the

SRA in relation to carboxylate anions than in relation to neutral molecules of unsaturated acids. Hence it follows that the SRA is an electrophilic anion[333], which differentiates it sharply from organic radical-anions[355].

VI. OTHER INORGANIC RADICAL-IONS

A large number of other relatively unstable inorganic radical-anions have been described. Although very little is known about the organic reactions of these species, some of them are of considerable interest for organic chemistry. These include the relatively unstable molecular halogen ions $X_2^{\cdot-}$. Presumably the $X_2^{\cdot-}$ radical-anions should arise in organic reactions with participation of halogens acting as electron acceptors. For example, the reaction of tetramethylhydrazine with iodine is treated in this way[356]:

$$Me_2NNMe_2 + I_2 \rightleftarrows Me_2NNMe_2 \ldots I_2 \rightleftarrows [Me_2NNMe_2]^{\cdot+} + I_2^{\cdot-} .$$

Another pathway leading to halogen radical-anions involves the reaction of the halide ion with the atomic halogen:

$$X^{\cdot} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X_2^{\cdot-}$$

($k_1 = 2.1 \cdot 10^{10}$ litre mole^{-1} s^{-1}; $k_{-1} = 1.1 \cdot 10^5$ s^{-1}; $K = 1.9 \cdot 10^5$ litre mole^{-1} (Ref.357) (X = Cl)).

In practice the $X_2^{\cdot-}$ radical-anions are usually generated by the radiolysis of aqueous solutions of alkali metal halides[358-361].

Halogen radical-anions are apparently effective oxidants[103]. The oxidation of bicarbonate or carbonate ions by the hydroxy-radical[362] or the $SO_4^{\cdot-}$ radical-anion[363] as well as the flash photolysis of the salt (XXVI) [364,365] lead to the radical-anion $CO_3^{\cdot-}$:

$$HCO_3^- (CO_3^{2-}) + {}^{\cdot}OH \rightarrow CO_3^{\cdot-} + H_2O\,(OH^-) \ ;$$

$$CO_3^{2-} \xrightarrow[-SO_4^{2-}]{SO_4^{\cdot-}} CO_3^{\cdot-} \ ;$$

$$\text{(XXVI)} \quad [Co(NH_3)_4CO_3]ClO_4 \xrightarrow{h\nu} CO_3^{\cdot-} + Co + 4NH_3 + ClO_4^- .$$

The pK for the equilibrium $HCO_3^{\cdot} \rightleftarrows H^+ + CO_3^{\cdot-}$ is 9.5.[366,367]

The chemical properties of the $CO_3^{\cdot-}$ radical-anion are of considerable interest, since its formation is to be expected in living organisms exposed to ionising radiation (from the hydroxy-radical and the bicarbonate anion). In addition, another possible pathway leading to the formation of the carbonate radical-anion may involve the photochemical oxidation of the carbonate ion by quinones[368].

It has been found that this radical-anion reacts with alcohols, abstracting an α-hydrogen atom[365], and with aromatic compounds[369]; in the latter case it apparently adds to the aromatic ring.

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Thus inorganic radical-anions and in the first place the oxygen and sulphate radical-anions, are extremely promising for synthetic and theoretical organic chemistry. The study of the properties of inorganic radical-ions constitutes an essential stage in the investigation of both photosynthetic and respiratory processes; without it, there can be no effective attempt at a functional modelling of these processes.

The chemistry of unstable inorganic radical-ions leads to new possibilities for the investigation of the mechanisms of reactions of organic substrates with inorganic reagents, including those of various heterogeneous-catalytic processes.

During the preparation of the review for the press, a number of interesting studies on the chemistry of the oxygen radical-anion were published[370-381].

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Association of Dye Molecules and Its Spectroscopic Manifestation

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Theoretical data for the influence of the association of the molecules of complex organic compounds (dyes) in solutions on their electronic spectra and other optical characteristics are examined and surveyed. The conditions for the formation of associated species and the influence of solvents, concentration, and temperature on this process are described. Methods for the determination of the association constants and the structure and compositions of the associated molecules are examined. The results of studies undertaken to investigate the luminescent associated dye species, their triplet states, and pathways leading to the deactivation of the electronic excitation are described. The nature of the forces which lead to the binding of the dye molecules in associated species is discussed and studies on the concentration-induced quenching of the luminescence of dye solutions are analysed.
The bibliography includes 197 references.

CONTENTS

I. Introduction 1076
II. Experimental study of association. Conditions for the formation of associated species and their structure 1076
III. Theory of the spectra of associated molecules 1080
IV. Luminescent associated species 1083
V. Triplet states of associated species 1085
VI. Association and concentration-induced quenching of luminescence 1086

I. INTRODUCTION

Numerous studies have been carried out during recent decades on the association of the molecules of complex organic compounds in view of both scientific interest in the nature of excited electronic states and their role in chemical and biological processes and photochemical reactions, and the extensive use of organic dyes in laser technology, in cine-phototechniques, and in other fields. For example, in the course of photosynthesis chlorophyll functions in an associated state and haemoglobin consists of four subunits, the haem groups being involved in a close interaction. Nitrogen-containing bases, forming part of nucleic acids and interacting with one another, give rise to a molecular aggregate. The study of various properties of complex molecules which exist in the monomeric state in solution is complicated by different types of intermolecular interaction and this is the reason why studies on association permit a deeper understanding of their intramolecular energetics.

One of the most important classes of compounds with a complex molecular structure, which are widely used in technology, are organic dyes. Dyes are unique agents capable of transforming light energy. Their extensive technical applications are in fact due to their photophysical properties–their ability to absorb light and transform it into radiation at other frequencies. These properties depend on many factors, including intermolecular interaction. The association of dye molecules has a significant influence on their photophysical properties, resulting either in a loss of capacity for luminescence or in an appreciable redistribution of the emitted energy.

The association of molecules of complex organic compounds has been studied in numerous investigations. Nevertheless, there is not yet a unanimous view in the literature on many problems, such as, for example, the quantitative relation between the migration of the excitation energy in dye solutions and quenching of the luminescence, which are closely related to problems of association. All the aspects of the spectroscopic manifestation of association have not been ultimately elucidated either.

The aim of the present review is to give an account of the association of dye molecules from the standpoint of the influence of this process on their photonics and the spectroscopic changes occurring in their aggregation. Associated dye molecules, which are stable in the ground state and which are formed in weak and intermediate interactions, are examined; aggregates produced by covalent bonding (the so-called intramolecular associated species) and problems associated with formation of excimers and and charge-transfer complexes are not considered.

II. EXPERIMENTAL STUDY OF ASSOCIATION. CONDITIONS FOR THE FORMATION OF ASSOCIATED SPECIES AND THEIR STRUCTURE

The procedures used to investigate the aggregation of complex organic molecules are extremely varied: methods based on the study of diffusion[1], conductivity[2], light scattering[3], polarography[4,5], and electron paramagnetic resonance[6]. Spectroscopic methods (spectrophotometric and luminescence methods) are most widely used and yield the most fruitful results. This review presents the results of spectroscopic studies of association.

The association of dye molecules has been observed in various solvents and its nature (degree and order of association and the structure of aggregates) depend significantly on the nature of the solvent. Dye molecules are very effectively associated in water[7-11] and in mixtures of polar and non-polar solvents[12-15]. In polar solvents, where dye molecules are strongly solvated, their aggregation occurs at high concentrations[16,17]. In non-polar solvents chlorophyll molecules associated even at low concentrations[18,19], but dyes do not usually dissolve in such solvents. A decrease of the temperature of the solution intensifies association[20-27].

In the majority of studies of the association of the molecules of complex organic compounds the authors observed the occurrence of aggregation in different solvents, calculated the monomer–dimer equilibrium constants and the

heat of association (the binding energy of the molecules), isolated the spectrum of the associated species, and determined the degree (fraction of associated molecules) and order (number of molecules in the associated species) of association.

The most typical three kinds of changes in the absorption spectra of dyes occurring when their molecules are associated are as follows: (1) the formation of a narrow band (cyanine dyes); (2) decrease of absorbance (thiazine dyes); (3) the splitting of the absorption band into two and more components (xanthene dyes, acridine compounds, etc.).

Fig. 1 presents the absorption spectra of solutions of rhodamine 6G for different concentrations in an ethanol–carbon tetrachloride mixture. The changes in the spectra with increasing dye concentration indicate the formation of associated rhodamine species.

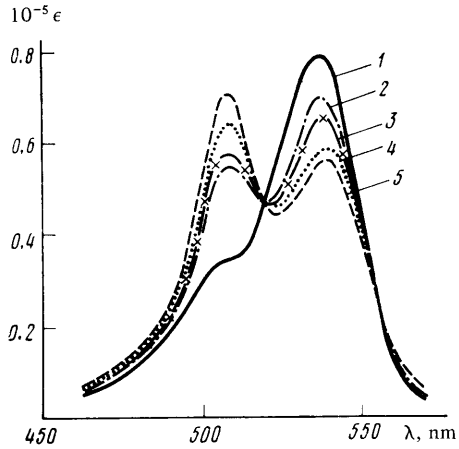


Figure 1. The absorption spectra of solutions of rhodamine 6G in a mixture of ethanol and carbon tetrachloride as a function of concentration (M): 1) 1.0×10^{-4}; 2) 6.4×10^{-4}; 3) 1.0×10^{-3}; 4) 2.5×10^{-3}; 5) 4.0×10^{-3}.

Association is most pronounced in aqueous solutions. Scheibe and coworkers[28,29] observed the formation in water of involved complexes of cyanine dyes, which have come to be called "Scheibe polymers". An increase of the concentration of these compounds leads to the appearance of a new very intense absorption band with $\lambda_{max} =$ 574 nm in the absorption spectra at $c = 4 \times 10^{-3}$ g ml^{-1}. The half-width of this band proved to be approximately six times smaller than that in the absorption spectrum of the dilute solution. The viscosities of such concentrated solutions are greatly increased; these phenomena are fully reversible on dilution or on heating of the solution. Förster[30] proposed a model for the Scheibe polymers, according to which the planar dye molecules are arranged in a row at equal distances from one another and have translational symmetry. If the oscillators of the individual molecules forming the polymer have the same amplitudes and vibration phases, the latter are added together, which gives rise to a resultant transition moment differing from the moment of each component oscillator; according to Förster, this should result in the appearance of a new absorption and luminescence band. The small width of this band is due to the fact that translational symmetry obtains only along the polymer axis. In this case the width is determined by the corresponding transitions allowed by selection rules. The formation of associated cyanine molecules has been observed not only in water but also in many organic solvents[31], for which narrow absorption bands appeared gradually with increased concentration of cyanine solutions and not abruptly; with increase of concentration, the association process is merely strongly accelerated. Aggregates of cyanine dyes, which are formed in aqueous ethanol solutions[32,33] also have an ordered layer structure with a definite distribution of anions between individual layers. This conclusion was based on a study of the concentration-induced changes in circular dichroism spectra and ultraviolet absorption spectra.

The concentration and temperature effects in aqueous solutions of rhodamines 3B and 6G have been investigated by Levshin and Baranova[7], who studied the influence of pH on the state of the dye and described a method for the determination of the degree of association in its solutions. The association of Congo Red, Methylene Blue, Crystal Violet, and other dyes in water and aqueous alcoholic solution has been studied[5,34,35] by both spectroscopic and polarographic methods. The authors of these investigations obtained conflicting results for the compositions of the associated species. Thus, according to their data, associated Crystal Violet species consist of 5–6 molecules. However, it has been noted[9] that this dye forms a mixture of associated species and the number of molecules in such association complexes increases with concentration. An estimate of this number based on diffusion measurements[1] yielded 18 molecules, while for substances analogous to those investigated by Hiroshi et al.[32] an association order of 2–3 was obtained.

With increase of dye concentration and with decrease of temperature, the equilibrium between monomeric dye molecules and associated molecules shifts towards the latter. A number of studies have been made on these problems for xanthene dyes in aqueous solutions[17,36-42]. On the assumption that the associated species of these dyes are dimers, methods have been developed for the isolation of their absorption spectra, the monomer–dimer equilibrium constants have been calculated, and chemical relaxations have been studied.

The influence of the solvent on aggregation processes is determined by the extent to which it promotes or hinders the combination of dye molecules by surrounding them with a solvation shell. The addition of organic solvents to aqueous solutions has a significant influence on the association of dye molecules[8,43-45], suppressing the latter. Absorption bands due to dimers and trimers have been observed in the absorption spectra of aqueous glycerol solutions and pyronine and fuchsine as a function of concentration ($5 \times 10^{-2} - 5 \times 10^{-6}$ M) at room temperature and at 80 K;[43] these spectroscopic changes can be satisfactorily accounted for within the framework of exciton theory.

The formation of associated species in aqueous solutions has been observed for thiazine dyes[46] (dimers), Acridine Orange, and Methylene Blue[47] (complex polymers), and for Bonadur Red[48] (dimerisation via hydrogen bonding with a heat of dimerisation of approximately 6 kcal mole^{-1}).

Associated species can also be formed from unlike molecules. However, the problem of association of unlike molecules of complex organic compounds has been inadequately investigated. There have been a few studies devoted to this subject[40,49-51]. It has been established[51]

that, with increase of the concentration of Acridine Orange and rhodamine 6G in aqueous solution of Methylene Blue, the absorbance falls both in the band of Methylene Blue (λ_{max} = 664 nm) and in the bands of Acridine Orange (λ_{max} = 492 nm) and rhodamine 6G (λ_{max} = 526 nm); in the first case new absorption bands do not arise. Such behaviour of the absorption spectra of the above systems indicates association of unlike species (their bond energy is 12 kcal mole^{-1} in the first case and 7 kcal mole^{-1} in the second). The study of such aggregates is the significant interest for the further development of the theory of the association of complex organic molecules.

The problem of whether or not dye molecules associate in solutions with a polar organic solvent remained unsolved for a long time. The difficulty was that the electronic absorption spectra of such solutions do not vary over a wide concentration range[52]. However, by measuring the concentration dependence of the average molecular weight of rhodamine dyes in alcoholic solutions, it was established[16] that in this case association takes place also. This was demonstrated indirectly in another study[53]. The degree of association in such highly concentrated solutions reaches 16%.[16] Associated species in alcoholic solutions of rhodamine dyes were detected also by EPR.[6] Nevertheless, studies where it is concluded that there is no aggregation of dye molecules in alcoholic solutions in view of the lack of any changes in the absorption spectra are still being continued[37,54]. The reason for this is that the degree of association of dye molecules in polar organic solvents is insignificant[16] and the absorption spectrum of the resulting associated species is similar to that of the monomer.

The study of the role of the anion in the association process[55,56] in various solvents showed that it does not have a significant influence on the aggregation of dye molecules. On the other hand, the structure of dye molecules has a strong influence on the development of association[57-59], which will be discussed below. The influence of temperature on the association of xanthene dye molecules has been studied[26,60-62]. Investigation of the ultraviolet absorption spectra of acridines in the range from 20° to −140°C [63] led to the conclusion that on cooling dimerisation takes place with participation of the hydrogen bonds in the NH groups.

The study of the association of dye molecules usually reduces to the determination of a number of constants, among which the number of molecules in the associated species n and the aggregation constant K_n are important. These constants are difficult to determine from spectroscopic data, since the number of unknowns is greater than the number of equations which can be set up. These difficulties have been overcome[20] with the aid of the equation

$$\lg [C_0(\varepsilon - \varepsilon_1)] = n \lg [C_0(\varepsilon - \varepsilon_n/n)] + \lg [K_n n (\varepsilon_1 - \varepsilon_n/n)^{1-n}], \quad (1)$$

where ϵ is the observed absorbance at a specified wavelength, ϵ_1 and ϵ_n are the absorbances of the monomer and the associated species, and C_0 is the overall concentration of the dye in solution. By plotting $\lg C_0(\epsilon - \epsilon_1)$ against $\lg C_0(\epsilon - \epsilon_n/n)$, it is possible to determine the order of the aggregation n from the slope of the resulting straight line and K_n can be found from the intercept on the ordinate axis. The difficulty of this method lies in the fact that one must know exactly the values of ϵ_1 and ϵ_n/n.

Other graphical methods have been proposed[64]. The authors call these procedures the "method of maximum slope" and the "method of optimum deviation". These methods make it possible to determine the molar extinction coefficient and the number of molecules in the dye aggregates provided that there is equilibrium between the monomers and associated species, and the absorption spectrum of the monomers is known. Comparison of the two methods[65] showed that they yield concordant results. A method for the determination of the order of association of dyes involving the study of the deviation from Beer's law has been described[66].

The knowledge of the geometrical structure of aggregates is of great interest for the theory of the association of complex molecules. In particular, it can help in the elucidation of the nature of the forces binding dye molecules into associated species. Although the geometry of such species can apparently be extremely varied in different instances, in theoretical calculations it is usually assumed that they have an ordered structure[67-70]. The spectra of solutions of dyes in which their molecules are associated also very often indicate the existence of such order. For a "sandwich" structure of the aggregates, the angle between the planes of the associated molecules φ is calculated from the formula[67,71-76]

$$\mu_s/\mu_d = (1 + \cos\varphi)/(1 - \cos\varphi), \quad (2)$$

where μ_S and μ_d are the electronic transition moments for the short- and long-wavelength absorption bands of the dimer, which are calculated with the aid of the relation $\mu^2 = 1.09 \times 10^{-19} \int \alpha(\nu) d\nu$ [$\alpha\nu$ is the absorption spectrum of the corresponding band]. The transition moments are related to the oscillator strength f by the expression

$$f = 8\pi^2 m_e c g \nu \mu^2 / 3he^2 \quad (3)$$

where ν is the frequency (cm^{-1}), m_e and e are the electronic mass and charge, g is the degeneracy of the excited state, and $\alpha(\nu)$ is the absorption spectrum of the corresponding band. The resolution of the spectrum of the dimer into the long-wavelength and short-wavelength bands presents a definite difficulty. Methods for such resolution in specific but practically important instances have been developed[77,78].

In order to solve the above problems, it is also necessary to know the concentration of the associated species in solution. This can be determined from absorption spectra[79] and by measuring the number-average molecular weight[16]. A method has been proposed[80] for the determination of the concentration of dimers and the equilibrium constants for their formation based on the measurement of the concentration dependence of the degree of polarisation and the luminescence quantum yield. A satisfactory agreement of the results obtained by this method and spectrophotometrically has been demonstrated for water–glycerol mixtures. The method is convenient when the dependence of the absorption spectra on concentration is insignificant.

The aggregates formed are very often treated as dimers in studies of association. However, when the order of the association is determined, experiments shows that this is by no means always the case. For example, in the study of concentrated solutions of 1,1-diethyl-2,2-cyanine bromide at low temperatures[81] it was possible to resolve the individual absorption bands referring to dimers (483 nm), trimers (465 nm), and tetramers (458 nm). On the basis of spectroscopic data, it was then concluded that several forms of aggregates exist: aggregates with a perpendicular disposition of the interacting molecules relative to the long axis of the aggregate and aggregates consisting of left- and right-hand helicoidal structures with eight monomers per turn of the helix. The study of the absorption and luminescence spectra of fluorescein, eosin, erythrosin, pyronine, and fuchsin at

different concentrations and temperatures[43,82] showed that, with increase of the concentration of dyes, characteristic changes occur in the spectra due to the formation of dimers and more complex aggregates. Electronic spectra for aggregates acquire partial exciton character.

The study of the association of rhodamines C, 3B, and 6G and of unsubstituted rhodamine in various solvents at 9° and 22°C [17,83,84] made it possible to obtain the aggregation constants and to reach a conclusion about the geometrical disposition of the molecules in the dimers ("in a stack" in water and "end to end" in ethanol). The study of azulenes in isopentane–methylcyclohexane glasses at 77 K and $c \simeq 10^{-3}$ M showed[85] that dimers are formed and their energy levels were calculated. The luminescence of such dimers was not detected. It has been established[16,26] that, in concentrated alcoholic solutions of rhodamine dyes at room temperatures, and on cooling, involved associated species comprising six dye molecules are formed on cooling. The molecules are arranged "end to end" and the angle between them decreases with decrease of the solution temperature. The geometrical structure of the aggregates of cyanine dyes has been studied[86] in various solvents by electron microscopy, optical microscopy, X-ray diffraction, and absorption spectroscopy. The results suggest that the planes of the molecules in the associated species are parallel, i.e. the aggregates have a "sandwich" structure. The authors separated the absorption bands for small aggregates up to pentamers.

On the basis of a study of the electronic spectra of a number of compounds in EPA (a mixture of ether, pentane, and ethanol), an interesting hypothesis has been put forward[87], namely that the spectroscopic changes on passing to dimers are due mainly to a change in the geometry of the monomer itself and that the splitting of the levels plays a secondary role. However, this hypothesis can be hardly regarded as sufficiently well founded.

The knowledge of the geometrical structure of the associated species may prove to be important for the elucidation of the nature of the forces responsible for the association of dye molecules. Quite inadequate attention has been devoted to this problem in the literature, evidently owing to the great complexity of the inter-molecular interactions in solutions of organic compounds. It has been concluded[88] that thionine and Methylene Blue dimers are formed as a result of van der Waals forces. The free energy of the dimerisation of Methylene Blue in water at 26.7°C was found to be 4.9 kcal mole^{-1}.

According to the theory of intermolecular interactions[89,90], the attraction energy of two identical molecules with a long-wavelength absorption band having a maximum at λ_0 is proportional to $f^2\lambda_0^3$, where f is the oscillator strength. Since f and λ_0 are large for dyes, the attraction forces between their molecules should also be greater when the latter approach one another sufficiently closely than for the corresponding colourless forms. These forces combine dye molecules into dimers or more complex associated species. Terms taking into account dipole–quadrupole and quadrupole-quadrupole interactions, evaluated by Margenau[90], may be added to those for the London dipole–dipole interaction[89] in the case of dyes.

Calculations by Davies and Coulson[91] showed that, for large molecules with extensive π-electron clouds, the dispersion forces, which make the greatest contribution to the van der Waals molecular interaction energy, may reach large values (tens of kcal mole^{-1}) for short intermolecular distances. These calculations were carried out for molecules which were simple compared with dyes.

The theory of van der Waals forces was constructed on the assumption that the distances between the interacting molecules are greater than their transverse dimensions[92,93].

For small intermolecular distances, characteristic of highly concentrated solutions, forces which decrease faster than as $1/R^6$, for example, forces associated with the quadrupole interaction, may become important also. It is usually believed that the energy of the van der Waals interaction does not exceed 2 kcal mole^{-1} for dye molecules[10,11]. However, this cannot apparently be regarded as a firmly established theoretical fact (for large molecules of the type of dyes, the bond energy has not been calculated rigorously) or as an accurate experimental result (the attempts at a quantitative test of the theory of universal molecular forces failed to yield sufficiently convincing results, since they were based on the measurement of integral effects which depend on the interaction of many molecules at different distances[94]). The view according to which dye molecules associate via van der Waals forces is shared also by many other workers[30,31,95–99], who investigated the association of the molecules of various compounds in different solvents.

Another view is that the association of dyes takes place via hydrogen bonding. It has been shown for a large number of dyes that the hypothesis of the major role of dispersion forces in the formation of associated species conflicts with many experimental facts. These are in the first place the strong dependence of the efficiency of the association process on the nature of the solvents employed and the structure of the dye molecules[13,93,100–102]. Concentration-induced changes in the absorption spectra, indicating the association of dye molecules in solutions, have been observed for compounds whose molecules have active N–H groups. The spectra of solutions of dyes whose molecules have no such groups do not change in the same solvents with increase of their concentration, which indicates the absence of association according to the authors of the above investigations.

Hydrogen bonds can be formed either directly between dye molecules or the latter may be combined with the aid of water molecules, which play the role of intervening bridges. The presence of intermolecular hydrogen bonds $\rangle$N–H...O=C$\langle$ and $\rangle$N–H...O$\langle$ has been established for rhodamine 6G also on the basis of infrared absorption spectra[103–105]. In chloroform–carbon tetrachloride mixtures the intensity of the absorption band due to free N–H vibrations (ν_{max} = 3445 cm^{-1}) decreases appreciably and the intensity of the broad band, which is appreciably displaced towards longer wavelengths (ν_{max} = 3200 cm^{-1}), increases in the spectrum of this dye with increased content of the non-polar component. This indicates the appearance of N–H vibrations perturbed by hydrogen bonding. Analogous changes occur in the infrared spectra of the solutions with increase of the dye concentration and with decrease of solution temperature[106].

Analysis of numerous experimental data obtained for solutions of xanthene and triphenylmethane dyes[105] showed that their associated species are formed on combination of two ion pairs via hydrogen bonds between the N–H group of the cation in one pair and the anion of another:

$$RN^+—H \ldots A^-RN^+—R.$$

The fundamental role of hydrogen bonds in the association of dye molecules in aqueous and aqueous alcoholic solutions as well as in binary mixtures of a polar and

non-polar solvent has also been indicated in other studies[60,107,108].

However, one should note that in the above studies it has been suggested that the polar organic solvents there is no association of dye molecules[109-111] because the active N–H groups of dyes are "occupied" by solvent molecules. Further study of this problem showed[16] that molecular associated species containing active N–H groups (rhodamine G, 6G, and others) and without active groups (rhodamine C, 3B, S, and others) are formed at high dye concentrations, the association in the former case beginning at lower concentrations. This apparently shows that association via hydrogen bonding takes place to a definite extent also in alcoholic solutions. In the second case associated species are evidently formed via van der Waals forces. This is indicated also by the finding that the associated species in such solutions are involved (approximately 6 molecules in a single aggregate). The energy of the bond between two molecules in such associated species is approximately 4 kcal mole^{-1} in all rhodamines[26], i.e. approaches the energy of the hydrogen bond.

In some studies it has been suggested that hydrophobic forces[107] and the interaction of dye molecules with the accompanying anions[56,112] are responsible for their association. The study of rhodamine dyes showed that the tendency towards association increases with increasing number and size of alkyl substituents[54].

The problem of the nature of the forces responsible for the association of dyes must apparently be solved in each specific instance in its own way. There is no point in extending the results for several examples to all cases. On the other hand, van der Waals forces, being universal, always act between dye molecules at a sufficiently short distance.

However, theories attempting to explain the spectroscopic changes occurring in the association of dye molecules do not take into account the nature of the intermolecular interactions.

III. THEORY OF THE SPECTRA OF ASSOCIATED MOLECULES

Förster's theory[30,113], describing the molecular properties of aggregates has been developed solely for dimers. It is assumed that the associated species consist of monomeric dye molecules whose planes are parallel to one another. Such dimeric molecules should possess an additional twofold symmetry axis apart from the symmetry elements of the monomer. The transition moments (oscillators) of these molecules are also parallel for the visible part of the spectrum. In consequence of thermal vibrations or structural assymmetry, the parallel arrangement may break down. For such a model, the oscillators of both molecules can be represented by two normal vibrations at different frequencies, each involving separate oscillators with the same amplitudes. However, the vibrations of one set of oscillators have the same phase, while those of the other set differ by 180°, i.e. the vibrations can be both symmetric and antisymmetric.

The vibrations of individual oscillators can be represented schematically as follows:

$$\rightleftarrows \quad \rightleftarrows \quad .$$

Symmetric vibrations give rise to a resultant non-zero dipole moment; for antisymmetric vibrations, the changes in the moments of individual oscillators cancel out. On absorption and emission of light, only symmetrical vibrations of the dipole are therefore excited, while the antisymmetrical vibrations are inactive. The two types of vibrations have different intrinsic frequencies due to the electric coupling of the two oscillators. Such coupling enhances in the case of the symmetric vibrations and weakens in the case of the antisymmetric vibration the force which restores the oscillators to the equilibrium position. As a result, compared with the vibration of the monomeric oscillator, the symmetric coupled vibration has a higher intrinsic frequency and the antisymmetric vibration has a lower frequency.

Thus, when two molecules approach one another, the electronic transition band is split. However, for the antisymmetric vibration the overall dipole moment of the dimer is unchanged and the absorption spectrum manifests only the transition associated with the symmetric vibrations of the oscillators, i.e. vibrations having a higher frequency. This leads to the experimentally observed hypsochromic shift of the absorption band on dimerisation of dye molecules. Since the transition corresponding to the antisymmetric vibrations, i.e. the transiton from the lowest excited level, is forbidden, the dimers do not luminesce.

This hypothesis cannot explain the finding that the spectra of the dye dimers frequently consist of two bands. According to Förster's theory the observation of such dimers would be impossible in view of the metastability of the excited state with the lower energy. Förster therefore suggests that in such cases the bond energy in the associated species is low and the oscillators of both molecules fail to attain a parallel arrangement in the ground state.

By applying the free electron model to a system consisting of two monomers, each of which has two electronic levels in the free state, Nikitin[114] obtained identical splittings of the energy levels of the ground and excited states, between which four electronic transitions are possible. Two of these have the same energy, equal to the transition energy in the monomer. The other two transitions are displaced–the frequency of one is smaller and that of the other greater than the frequency of the transitions in the monomer. The probabilities of the last two transitions proved to be much greater than the sum of the probabilities with identical frequencies. Thus Nikitin's calculation predicts qualitatively the splitting of the absorption band of the monomers into two components on formation of dimers. Förster's and Nikitin's theories explain only the displacement and splitting of the absorption spectrum on association of dye molecules. They do not yield quantitative relations for the calculation of the splittings.

Simpson and coworkers[115,116] carried out a quantum-mechanical calculation on dye dimers assuming that the molecular planes of their cations in the dimer are parallel ("sandwich" structure) and neglecting the interaction between the components corresponding to the monomers of the electronic wave functions for the ground state and the doubly degenerate first excited state. Thus it is suggested that the wave function of the ground state of the dimer has the form $\Psi_1\Psi_2$ and that of the excited state is $\Psi_1^*\Psi_2$ and $\Psi_1\Psi_2^*$, where Ψ_1 and Ψ_2 are the wave functions of individual molecules *1* and *2* forming the dimer and the asterisk denotes electronic excitation.

In their calculations Simpson and coworkers used the following expression for the molecular interaction potential:

$$V = (-2\Sigma z_1 \Sigma z_2 + \Sigma x_1 \Sigma x_2 + \Sigma y_1 \Sigma y_2)\, e^2/R^2, \qquad (4)$$

where e is the electronic charge, R the distance between the molecules, and x, y, and z are the coordinates of the electrons of the corresponding molecules. The exact wave function for the excited state is

$$\Psi_{\pm} = 2^{-1/2}(\psi_1^*\psi_2 \pm \psi_1\psi_2^*). \quad (5)$$

Simpson and coworkers[115,116] showed that, in the case of a strong interaction of the molecules of dyes *1* and *2*, the interaction energy in the dimer is given by the following expression in terms of the dipole approximation:

$$W_{\pm} = \pm \bar{m}_1\bar{m}_2/R^3, \quad (6)$$

where, for example, the x component of the dipole moment of the transition $\bar{m}_1$ can be written as follows:

$$(m_1)_x = e\int \psi_1 \Sigma x_1 \psi_1^* d\tau_1. \quad (7)$$

The transition moment for absorption by the dimer is given by the expression

$$\bar{m}_{\pm} = 2^{-1/2}(\bar{m}_1 \pm \bar{m}_2). \quad (8)$$

If the disposition of molecules in such that $\bar{m}_1 = -\bar{m}_2$, then the transition moment (on absorption of a light quantum) to the lower of the excited split levels with an energy W_+ is zero and the moment of the transition to the higher of the levels with an energy W_- is $2^{1/2}m_1$, which corresponds to an increase of the absorption intensity by a factor of two compared with a monomeric molecule.

Simpson and coworkers[115,116] explained the agreement between their model and experiment by the fact that the short-wavelength absorption band in the spectrum of the dimer is usually more intense than the long-wavelength band: on the other hand, the appearance of the latter can be accounted for by the fact that the molecular planes of dyes in the aggregate are not rigorously parallel. In their model the distance between identical molecules in the dimer is expressed in terms of the energy of the splitting of the levels by the formula

$$\Delta W = W_- - W_+ = 2|\bar{m}_1|2/R^3. \quad (9)$$

De Voe[117,118] developed a semiclassical theory of the electronic absorption spectra of associated species with weak bonding, where the Born–Oppenheimer approximation was used in the electronic and vibrational components as the zeroth approximation to the wave function for each monomer. Using the first-order perturbation theory, De Voe derived equations relating the extinction coefficient of the band due to the associated species to the parameters of the spectra of its constituent monomers.

De Voe's fundamental hypothesis is that the optical properties of each monomer can be described by one or several one-dimensional complex polarisabilities with different directions of polarisation and different frequency dependences. The associated species is characterised by M different polarisabilities $\alpha_i^0(\nu)$ of N monomers ($M \geqslant N$) and the directions of their polarisations are specified by unit vectors $\mathbf{e}_i$, where i varies from 1 to M. In quantum theory polarisability corresponds to the dipole moment of the transition from the ground to the excited electronic state. The vector $\mathbf{e}_i$ has the same direction as the electronic moment of the transition $\boldsymbol{\mu}_i^0$.

It is assumed that the associated species consists of N monomers and that it is small compared with the wavelength of the incident light. On can therefore neglect the lag effect and can assume that the electric field of the incident light is the same within the limits of the associated species. The polarisability of each monomer is determined by the strength of the local field in which the monomer is located (the field of the incident light plus the field due to other monomers). The real component of the polarisability describes the polarisation in phase with the electric field of the incident light and the imaginary component describes the out of phase polarisation causing the absorption of light.

If $\epsilon_i(\nu)$ is the molar extinction coefficient of an isolated monomer, then the real and imaginary components of $\alpha_i^0(\nu)$ are given by the following equations:

$$\mathrm{Re}\,\alpha_i^0(\nu) = \frac{6\cdot 2303c}{8\pi^3 N_0}\int \frac{\varepsilon_i(x)\,dx}{x^2-\nu^2} \equiv R_i(\nu), \quad (10)$$

$$\mathrm{Im}\,\alpha_i^0(\nu) = -\frac{3\cdot 2303c}{8\pi^2 N_0}\cdot\frac{\varepsilon_i(\nu)}{\nu} \equiv I_i(\nu), \quad (11)$$

where c is the velocity of light and N_0 the Avogadro number. The principal value of the integral is used.

If the aggregate is in the field $\mathbf{E}$ of plane-polarised light at a frequency ν, then each of the N monomers undergoes polarisation, which depends on the incident field and the field of the other monomers. The complex amplitude of the induced moment of the polarisability of an individual monomer can be formulated as follows:

$$m_i(\nu) = \alpha_i^0(\nu)\left[\mathbf{e}_i\mathbf{E} - \sum_{j=1}^{M} G_{ij}m_j(\nu)\right]. \quad (12)$$

The expression in brackets represents the amplitude of the local field along $\mathbf{e}_i$. The above equation expresses the induced moment of the polarisability of the ith monomer as a linear function of the induced moments of all other monomers in the aggregate. The interaction coefficient G_{ij} is interpreted as the energy of the Coulombic interaction between two point dipoles with dipole moments oriented along $\mathbf{e}_i$ and $\mathbf{e}_j$. In terms of the point dipole approximation, these coefficients are given by the expressions

$$G_{ij} = r_{ij}^{-3}[\mathbf{e}_i\mathbf{e}_j - 3(\mathbf{e}_i\mathbf{e}_{ij})\mathbf{e}_j\mathbf{e}_{ij})], \quad (13)$$

where $\mathbf{e}_{ij}$ is the unit vector along the line connecting the ith and jth monomers and r_{ij} is the distance between them.

For aggregates with an appreciable interaction between the monomers, De Voe[117,118] used the following expression for the density of the transition:

$$G_{ij} = V_{ij}/|\mu_i|\,|\mu_j|, \quad (14)$$

where V_{ij} is the energy of the Coulombic interaction between the charge densities of two molecules.

On solving M equations of type (12) written in matrix form, it is possible to calculate the optical properties of the aggregate. For a dimer with the same polarisability of each monomer ($N = M = 2$), the extinction coefficient is

$$\epsilon_d(\nu) = \sum_i\sum_{j\neq i}\varepsilon_i(\nu)\frac{1 - 2G_{12}R_i e_1 e_2 + G_{12}^2(I_1I_2 + R_j^2)}{[1 - G_{12}^2(R_1R_2 - I_1I_2)]^2 + [G_{12}^2(R_2I_1 + R_1I_2)]^2}. \quad (15)$$

De Voe[118] obtained a formula whereby G_{ij} can be expressed in terms of experimental quantities. For a dimer, G_{12} can be determined from the equation

$$\varepsilon(\nu) = \varepsilon^0(\nu)[1 - 2R(\nu)G_{12}(\mathbf{e}_1\mathbf{e}_2)],$$

where $\epsilon^0(\nu)$ and $\epsilon(\nu)$ are the extinction coefficients of the monomer and the dimer. Knowing the extinction coefficient of the monomer and the dimer for a specified value of ν and having calculated $R(\nu)$, it is possible to determine G_{12}.

The experimental study of the optical characteristics of the monomers, dimers, and more involved associated species of dyes[119-121] showed that there is only a qualitative agreement between De Voe's theory and experiment.

At the present time the main theory used to explain the spectroscopic features arising on aggregation of dye molecules is the exciton theory. The exciton model, developed by Davydov[122] for molecular crystals, has been used by a number of workers[67-70] to develop a theoretical method for the investigation of the spectra of associated species. For an aggregate comprising N molecules, the exciton band consists of N discrete levels. The dipole transitons in this system are allowed only for one or several (a small number equal to the number of molecules in the associated species) exciton states. The energy and wave function of the ground state of the aggregate are the same as for the monomers.

The wave function of the ground state of the dimer is

$$\Psi_0 = \psi_1 \cdot \psi_2, \tag{16}$$

where Ψ_1 and Ψ_2 are the wave functions of the ground state of the free monomer. The Hamiltonian of the dimer is

$$H = H_1 + H_2 + V_{12}, \tag{17}$$

where H_1 and H_2 are the Hamiltonians of the isolated molecules 1 and 2 and V_{12} is the intermolecular interaction potential (the Coulombic potential represented approximately by point dipole terms in the point-multipole expansion). The energy of the ground state of the dimer is obtained from the Schrödinger equation

$$E_0 = \int\int \psi_1\psi_2 H \psi_1\psi_2 \, d\tau_1 \, d\tau_2 \tag{18}$$

or

$$E_0 = E_1^0 + E_2^0 + \int\int \psi_1\psi_2 (V_{12}) \, \psi_1\psi_2 \, d\tau_1 \, d\tau_2. \tag{19}$$

The last term corresponds to the van der Waals interaction energy between the ground states of molecules *1* and *2* and E_1^0 and E_2^0 are the energies of the ground states of the isolated molecules.

The wave functions of the excited state of the dimer are written in the following form:

$$\Psi_E = r\psi_1^*\psi_2 + s\psi_1\psi_2^*, \tag{20}$$

where Ψ_1^* and Ψ_2^* are the wave functions of the excited state (with the energies E_1^* and E_2^*) and r and s are coefficients which must be determined. The Schrödinger equation for the excited state is

$$H(r\psi_1^*\psi_2 + s\psi_1\psi_2^*) = E_E(r\psi_1^*\psi_2 + s\psi_1\psi_2^*). \tag{21}$$

On multiplying the two sides of this equation by $\Psi_1^*\Psi_2$, integrating with respect to the coordinates of molecules *1* and *2*, and repeating this process for $\Psi_1\Psi_2^*$, we arrive at two equations containing terms which are symmetrical with respect to sub-scripts *1* and *2*:

$$\begin{aligned} H_{11}(=H_{22}) &= \int\int \psi_1^*\psi_2 H \psi_1^*\psi_2 \, d\tau_1 \, d\tau_2, \\ H_{12}(=H_{21}) &= \int\int \psi_1^*\psi_2 H \psi_1\psi_2^* \, d\tau_1 \, d\tau_2. \end{aligned} \tag{22}$$

The determinant of the coefficients r and s in these equations is zero for non-trivial solutions:

$$\begin{vmatrix} H_{11} - E_E & H_{12} \\ H_{21} & H_{22} - E_E \end{vmatrix} = 0. \tag{23}$$

The roots E_E are given by the following expressions in view of the equivalence of the terms of Eqns. (22):

$$\begin{aligned} E_E' &= H_{11} + H_{12} \text{ for } \Psi_E' = 2^{-1/2}(\psi_1^*\psi_2 + \psi_1\psi_2^*), \\ E_E'' &= H_{11} - H_{12} \text{ for } \Psi_E'' = 2^{-1/2}(\psi_1^*\psi_2 - \psi_1\psi_2^*). \end{aligned} \tag{24}$$

Having calculated E_E' and E_E'', we have, by virtue of the orthogonality condition for the wave functions of each molecule,

$$\begin{aligned} E_E' &= E_1^* + E_2 + \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1^*\psi_2 \, d\tau_1 \, d\tau_2 + \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1\psi_2^* \, d\tau_1 \, d\tau_2, \\ E_E'' &= E_1^* + E_2 + \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1^*\psi_2 \, d\tau_1 \, d\tau_2 - \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1\psi_2^* \, d\tau_1 \, d\tau_2. \end{aligned} \tag{25}$$

The last term in Eqns. (25) describes the exciton splitting:

$$\mathscr{E} = \int\int \psi_1^*\psi_2 (V_{12}) \, \psi_1\psi_2^* \, d\tau_1 \, d\tau_2, \tag{26}$$

It becomes, in terms of the point dipole approximation

$$\mathscr{E} = \mathbf{M}_1\mathbf{M}_2/r^3 - 3(\mathbf{M}_1 \cdot \mathbf{r})(\mathbf{M}_2 \cdot \mathbf{r})/r^5 \tag{27}$$

and represents the energy of the interaction due to the exchange of the excitation energy between molecules *1* and *2* at a distance r. The third term in Eqns(25) is analogous to the corresponding term in Eqn. (19) and corresponds to the van der Waals interaction between the excited molecule *1* and the ground state of molecule *2*. $\mathbf{M}_1$ and $\mathbf{M}_2$ are the transition moments in molecules *1* and *2* and r is the vector directed from molecule *1* to molecule *2*.

The exciton model describes the resonance splitting of the excited states of complex molecules. The ground state is displaced relative to the ground state of the initial molecules solely due to the van der Waals interaction.

Here one considers different limiting cases of the intermolecular bond. The ratio of the force of the intermolecular electronic interaction between excited states and the force of the intramolecular vibronic coupling serves in practice as a criterion for the assessment of the intermolecular bond[116]. For a strong bond, the following ratio is used as a criterion:

$$2U/\Delta\varepsilon \gg 1, \tag{28}$$

where $2U$ is the width of the exciton band and $\Delta\epsilon$ is the width of the Franck–Condon band of the corresponding molecular electronic transition in the monomer. The opposite inequality has been suggested as a criterion for a weak bond:

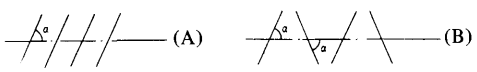
$$2U/\Delta\varepsilon \ll 1. \tag{29}$$

In the case of a strong bond, the electronic and vibrational wave functions are separated by the Born–Oppenheimer method. The absorption spectra of the dimer will be split if even one of the components of the electronic transitions is prohibited and is not shown in the spectrum. For a linear polymer of N molecules, the interaction of the latter leads to an exciton band consisting of N discrete exciton states. The selection rules for linear polymers have been developed by McRae and Kasha[67]. The bands of the resolved components then become very narrow, since excitation is in this case "smeared" over many molecules and each molecule has approximately the same electronic structure as the molecule in the ground state, i.e. the Franck-Condon principle allows in this case only the non-vibration 0–0 electronic transition.

A weak bond corresponds to the nonresolvability of the molecular wave functions by the Born–Oppenheimer method. In the limiting case of a weak bond no change in the spectral band is observed, but effects such as hypochromism or hyperchromism may be manifested.

The case of an intermediate bond constitutes an unsolved problem in exciton theory. Here one can observe a general distortion of the band contour.

McRae and Kasha[67] examined associated dye molecules having the following structures:



The theoretical calculation presented by the authors predicts the splitting of the energy levels of the excited states of associated species comprising N molecules into N levles. The splittings are

$$\mathscr{E} = 4\,[(N-1)/N\,](m^2/r^3)\,(1-3\cos^2\alpha), \tag{30}$$

for structure (A) and

$$\mathscr{E} = 4\,[(N-1)/N]\,(m^2/r^3)\,(1+\cos^2\alpha) \tag{31}$$

for structure (B), where m is the transition moment for the monomer. An increase of the probability of intercombination transitions in the association of dye molecules has been predicted[67].

In later studies the exciton theory was refined and tested experimentally. Thus, theoretical calculations of the spectroscopic characteristics of stable anthracene dimers were made and a satisfactory agreement with experiment was demonstrated[123,124]. An asymptotic expression for the shape of the dimer absorption bands has been obtained[125] by the method of exciton theory for the case of strong interaction of complex molecules. Allowance for intermolecular vibrations in dimers[126] made it possible to introduce certain refinements into the form of their absorption spectra. The vibrational states of the monomers constituting the molecular aggregates were also taken into account in the exciton theory[127]. The vibronic interactions in aggregates have been examined[128-131]. In this case the theory includes a parameter taking into account the intramolecular vibrations of the monomers and a parameter characterising the extent of the interaction between them. The theory taking into account such interactions has been tested in detail in experimental studies[132-134] whose results have been surveyed[135]. An experimental test showed that the predictions of the theory hold rigorously only for certain values of its parameters, which do not alway correspond to real systems.

Using the molecular exciton theroy, the vibronic interactions in helical aggregates were investigated theoretically[136] and a study was made of the influence of intramolecular vibrations of the monomers on their electronic absorption spectra.

More refined experiments[137], designed to investigate the absorption and polarisation spectra of luminescent dimeric forms of rhodamine C at room temperature and 77 K (in this case LiCl was added to improve the vitrification of the solutions), showed that the exciton theory cannot account for the measured polarisation characteristics of the dimers, whose interpretation requires allowance for the vibronic interactions in the molecules of the test compound. These ideas were subsequently developed[138] and confirmed experimentally for associated rhodamine and acridine dyes.

Thus the existing theories explain qualitatively many features arising in the electronic spectra of complex organic compounds when their molecules undergo association and also describe many quantitative effects. However, they apply only to dimers and more complex aggregates with a specific configuration. Complex associated species with an arbitrary structure, which can be formed in concentrated solutions, are not described by these theories.

One should note that the overall Hamiltonian (17) used in the exciton theory for the dimer does not take into account the perturbing effect of the field due to solvent molecules on the associated dye molecules.

Furthermore, it has been shown[139] that the stability of the associated species depends on the solvation shell consisting of solvent molecules, i.e. the theory must take into account also this form of intermolecular interaction.

IV. LUMINESCENT ASSOCIATED SPECIES

Association of dye molecules leads as a rule to the loss of their luminescent properties. However, under certain conditions the associated species fluoresce. The study of luminescent associated species is of both scientific and spectroscopic interest. Thus elucidation of the causes of the radiationless degradation of the electronic excitation energy of associated molecules can lead to the solution of a more complex problem, which Vavilov formulated as follows[140]: "The main problem of the photoluminescence of solutions, which has still not been solved even in broad outline, involves the question why some molecules luminescence while others do not". A study of the conditions governing the formation of luminescent associated species may help to elucidate the pathways whereby their electronic excitation energy is exchanged and the nature of their electronic spectra.

When non-luminescent associated species are formed, the absorption spectra of the dye solutions change, while their luminescence spectra do not undergo any alteration in form. Variable luminescence spectra and invariant absorption spectra would indicate the formation of excimers[141]. The formation of luminescent associated species in dye solutions is accompanied by the deformation of both their absorption spectra and their luminescence spectra.

In his study of the influence of concentration on electronic spectra, Levshin observed[142] that an increase of the concentration of fluorescein and Rhoduline Orange in rock candy leads to appreciable changes in their luminescence spectra. He also showed that Acridine Orange in rock candy forms luminescent associated species at 20° and −183°C.[143] At 20°C, starting from $c = 10^{-3}$ g g^{-1}, the luminescence spectra of rock candy activated with acridine show a gradual weakening of the green emission band (λ_{max} = 534 nm) due to the luminescence of monomers and the simultaneous increase in the intensity of the emission band of the associated species (λ_{max} = 575 nm). The influence of the concentration of this compound on the electronic spectra and the duration and yield of luminescence in frozen alcoholic solutions has been studied[144] and it has been shown that, with increase of the concentration of acridine from 1.6×10^{-6} to 1.3×10^{-2} M, the maximum in the overall luminescence spectrum shifts by 110 nm to the red region and the form of the spectrum change markedly. The fact that the association of Acridine Orange molecules leads to a marked weakening of the intensity of the long-wavelength absorption band and to the intensification of the short-wavelength band suggested that the transition to the upper electronic state is prohibited to some extent in associated molecules, i.e. that the associated molecules have a higher symmetry than the monomer.

In contrast to the spectra of aqueous solutions of Acridine Orange, the formation of a new band in the luminescence spectrum of rock candy is extremely slow, although the deformation of the absorption spectra begins to appear in both cases at approximately the same concentrations[143] and the positions of the maxima in the luminescence spectra are the same. However, it follows from the deformation of the absorption and luminescence spectra of Acridine Orange in rock candy that the amount of associated species in such solid solutions is smaller than in aqueous solutions at the same concentrations.

Measurement of the dependence of the pH of the solutions on the concentration of acridines showed that the changes in the spectra are not associated with the ionisation of their molecules in solution, as observed by Levshin[145]. The concentration-induced changes in the spectra of acridines occurred in the region corresponding to the existence of their molecules in the form of singly charged ions and must be attributed to their association. At the same time, it has been shown[20,143,144] that the associated Acridine Orange species exhibit an appreciable phosphorescence. This is caused by the higher probability of the transition of dimers to the triplet state as compared with the monomers.

With increase of the concentration of Acridine Orange above 10^{-3} M in ethanol, bands at 600 and 629 nm arise in the luminescence spectrum and their intensity increases[146]. They have been attributed to the luminescence of the associated Acridine Orange species. Eosin, whose monomeric form has a luminescence maximum at 568 nm, fluoresces with λ_{max} = 603 nm when associated species are formed in alcohols[147].

The study of the fluorescence of associated acriflavins and rhodamine 3B species in various solvents[148] showed that, when dimers, trimers, and more complex aggregates are formed, their luminescence maximum is displaced further towards the red region. Analysis of the spectroscopic data showed that the luminescence spectra of associated species are broader and the degree of polarisation of their luminescence is smaller than for the monomers[62,149].

As noted above, Scheibe polymers belong to the class of luminescent associated species. The luminescence of polymerised solutions of cyanine dyes proved to be very sensitive to the presence of various luminescence quenching agents. Thus the addition of approximately 10^{-5} M catechol to a solution containing 0.2% of pseudoisocyanine chloride[150,151] leads to a sharp decrease of the intensity of the luminescence of the dye. This implies that the emission of light by the entire complex is affected when even one of the dye molecules forming the chain comes into contact with a molecule of the quenching agent. It has been established[152] that, by virtue of the migration of excitation energy along the entire polymer chain, one molecule of the quenching agent per 10^3–10^6 dye molecules is sufficient for appreciable quenching. This suggested that the electrons of individual molecules in such polymers form a single electron cloud.

Another form of luminescent species made up of dye molecules has been observed[153,154] and investigated in detail by Morozov and coworkers[21,22]. When aqueous and aqueous alcoholic solutions are cooled to approximately −30°C, the luminescence of rhodamines virtually vanishes. Further cooling leads to the appearance of a new luminescence band displaced towards longer wavelengths. The intensity of this "red" luminescence band increases on successive cooling of the solutions. The addition of glucose, thiamine hydrochloride, etc. to the solution increase the intensity of the "red" band, but the "yellow" does not vanish completely. The addition of polar solvents to the solution (alcohol, pyridine, acetone, etc.) greatly weakens the above effects. In this case the intensity of the "yellow" band changes only slightly when the temperature of the solution is reduced and a weak "red" luminescence band appears only at approximately −100°C.

The above results have been explained[152] on the basis that freezing aqueous solutions removes the prohibition on singlet–triplet transitions and the "red" band is due to the phosphorescence of the associated dye molecules. The introduction of various additives into the solution alters, according to the author[152], the probabilities of the $S^* \rightarrow T_1$ and $T_1 \rightarrow S_0$ transitions. However, the marked dependence of the observed effects on the dye concentration in solution[22] indicates their relation with intermolecular processes. Furthermore, the durations of luminescence are the same order of magnitude for both rhodamine C bands: $\tau_L \simeq 10^{-8}$ s; $\tau_{Cr} \simeq 4.5 \times 10^{-9}$ s.

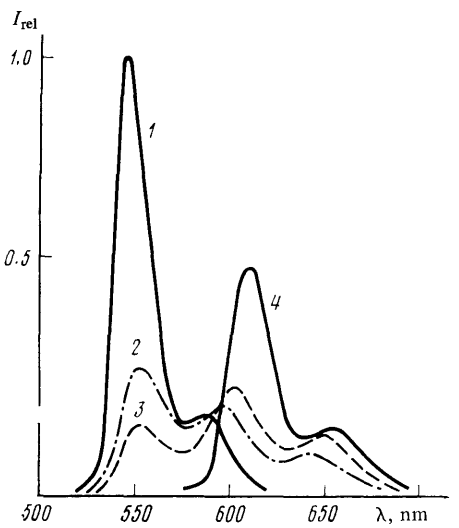


Figure 2. The luminescence spectra of solutions of rhodamine 6G in ethanol at −180°C as a function of concentration (M): 1) 1×10^{-5} (the I_{rel} scale has been reduced by a factor of 2); 2) 5×10^{-3}; 3) 1×10^{-2}; 4) 5×10^{-2}.

On the other hand, the difference between τ_L and τ_{Cr} for frozen solutions shows that different luminescence centres are responsible for the appearance of these bands.

The observed phenomenon has been explained[21,22] by the fact that the crystallisation of the solvent on freezing leads to the breakdown of the homogeneity of the solution, which decomposes into a solid phase consisting of the frozen solvent, not containing dye molecules, and a liquid phase to which virtually the entire dye is transferred together with the polar solvents added to the solution. The composition of the liquid phase differs from that of the initial solution by the markedly higher concentration of the dye. Cooling of such solutions leads to a gradual freezing out of water from the liquid phase and an

increase of the concentration of the dye in the latter, which creates favourable conditions for the formation of luminescent associated dye species. The authors[21,22] believe that the associated species formed under these conditions are dimers and that the "red" luminescence band is due to their fluorescence.

It was shown subsequently[6,24-26,62] that luminescent associated rhodamine dye species are formed also in purely polar solvents wihout breakdown of the homogeneity of the solutions on freezing. Not only dimers but also more complex associated species consisting of six molecules are formed in such solutions. Apparently in the instances described in the literature[21,22] the associated species are complex. The luminescence spectrum of such associated rhodamine 6G species in ethanol at −180°C is illustrated in Fig. 2. It consists of two luminescence maxima: the main maximum at $\lambda_{max} = 620$ nm and a lateral maximum at $\lambda_{max} = 670$ nm, which may constitute the manifestation of a vibrational structure. In the spectra of mixtures of polar and non-polar solvents at room temperature the luminescence maximum at $\lambda =$ 620 nm was attributed[155] to the phosphorescence of associated rhodamine dye molecules.

Luminescent associated rhodamine dye species have been detected at room temperature in mixtures of polar and non-polar solvents[156-161]. In this case the luminescence band of the associated molecules is displaced towards either shorter or longer wavelengths relative to the luminescence spectra of their monomeric molecules. The "red" luminescence of the associated species ($\lambda_{max} =$ 610 nm) has been observed for rhodamines in a mixture of chloroform (10%) and carbon tetrachloride (90%) at concentrations of approximately 5×10^{-4} M. The "blue" luminescence of the associated species of these dyes arises when the dyes are transferred to a non-polar medium by extraction from aqueous solutions with non-polar solvents (carbon tetrachloride). In the former case a long-wavelength maximum arises in the absorption spectra of the solutions, while in the latter case a short-wavelength maximum is generated. The formation of associated species comprising dye molecules in the above instances, which luminesce at room temperature, takes place as a rule in solutions whose homogeneity has been affected. Their structure and photoenergetics require further investigation.

V. TRIPLET STATES OF ASSOCIATED SPECIES

For many organic compounds, the triplet states of their molecules play the main role in radiationless electronic excitation energy exchange and in various photochemical reactions. The interest in the study of the triplet states of complex molecules is therefore understandable. However, the triplet states of associated molecules have been studied quite inadequately.

It is known from the theory of the electronic states of molecular aggregates[67,115,116,122] that, on molecular association, the singlet excited levels undergo appreciable changes, while the triplet levels change only slightly as a result of the spin-intercombination prohibitions.

The first experimental studies on the triplet state of associated dye molecules[162,163] confirmed these theoretical conclusions. A detailed study of the phosphorescence of associated Acridine Orange and rhodamine C species, dissolved in water and in a mixture of glucose and water, showed[162] that the maximum in the phosphorescence spectrum of acridine dimers is displaced towards longer wavelengths by approximately 100 Å relative to the phosphorescence line of its monomeric form. The values of τ for the phosphorescence of monomers and dimers then differ only slightly. For example, at room temperature $\tau_{phosph} = 10^{-2}$ s for the monomers and 6.3×10^{-2} s for the dimers of Acridine Orange, the ratio of these quantities remaining virtually unchanged on cooling the solutions. This shows that the probabilities of emission from the triplet levels and of the quenching of these levels are similar for the monomers and dimers. The phosphorescence yield for Acridine Orange dimers is much higher than for its monomeric form and depends on temperature to a greater extent. This can be explained by the mutual approach of the S_1^* and T_1 levels and the consequent increase of the probability of the $S_1^* \rightarrow T$ transition.

The phosphorescence spectrum of rhodamine C dimers in water with added glucose consists of two bands with maxima at approximately 620 and 690 nm. With decrease of temperature, the intensity of the short-wavelength band falls and that of the long-wavelength band increases. Since the maximum of the former band is close to that in the fluorescence spectrum of the dimers, the author[162] believes that it refers to α-phosphorescence, while the second band refers to the β-phosphorescence of the dimers.

Experimental evidence for the phosphorescence of the dimers of three organic compounds has been obtained[163]. The shape of the phosphorescence spectra of eosin, rhodamine C, and Acridine Orange in water at 77 K proved to be the same, but the phosphorescence spectrum of the dimers is displaced towards the red by 100–200 Å, relative to the phosphorescence spectrum of the monomers. The authors[163] concluded that both in the ground state of the associated species and in the triplet state the intermolecular distance is the same and that the decrease of energy by 300–500 cm^{-1} accompanying dimerisation is greater for the triplet state than for the ground state.

Spectroscopic methods make it possible to establish the probabilities of various transitions and the rate constants for many processes–emission and quenching of luminescence as well as intercombination transitions in organic molecules. Very few such measurements have so far been made for associated dye molecules and yet they are important not only for many practical tasks but also for the theory of association. The study of the redistribution of the probabilities of radiative and radiationless transitions, occurring when the dye molecules associate, is therefore of special interest. Such redistribution is caused particularly by a change in the relative disposition of the excited singlet and triplet levels when molecules associate.

Thus the influence of the association of eosin and erythrosin molecules at 80 K on processes involving the population and deactivation of the triplet state leads to an increase of the phosphorescence quantum yield relative to the fluorescence yield and a decrease of τ_{phosph} for solutions[164]. An increase of the concentration of solutions of these dyes in polar media results in a change of the probability of the intercombination transition and of the quenching of phosphorescence and has almost no influence on the probability of the radiative process.

New possibilities for the study of the triplet states of associated molecules of organic compounds arose following the discovery of the method of flash photolysis[165]. However, in contrast to the numerous studies of monomeric molecules by this procedure, the study of associated species is only beginning. Thus the triplet states and electronic excitation energy degradation processes in

associated rhodamine 6G–the dye most widely used in lasers†–have been investigated[166-168].

Associated rhodamine 6G species were obtained in two ways: (I)–concentrated solutions of the dye in a polar medium (aliphatic alcohols, acetonitrile, dimethyl sulphoxide, etc.) where diluted with a non-polar solvent (CCl_4, toluene, cyclohexane, etc.) so that the polar component did not exceed 0.2% of the volume of the solution; (II)–an aqueous solution of the dye was treated with polymethacrylic acid at the optimum concentration for the formation of associated species[169].

The results of the study of associated rhodamine 6G molecules reduce to the following findings. In binary mixtures dimers and complex associated dye species containing 15–20 molecules are formed. The associated species obtained by the second method consist of approximately 10 monomeric rhodamine molecules. The S_1^*-T splitting then depends on the order of the association. For example, the triplet level of rhodamine 6G dimers is higher ($14\,930\ cm^{-1} < E_T < 18\,400\ cm^{-1}$) than in more complex associated species ($14\,930\ cm^{-1} < E_T < 16\,800\ cm^{-1}$), while the positions of the triplet levels of the monomers and complex associated species are virtually the same[166]. The S_1^*-T splitting is directly related to the efficiency of the various pathways involved in electronic excitation exchange. For dimers, which are formed in solutions containing up to 80% of the non-polar component, there is a direct population of their triplet levels on pulse excitation. The luminescence quantum yield for the dimers is close to zero and the degradation of their singlet excitation energy takes place by a radiationless pathway as a result of an internal transition, which has a quantum yield $B_{it} \simeq 0.7$ and an intercombination transition whose quantum yield $B_T \simeq 0.3$.

In contrast to dimers, more complex associated rhodamine 6G species of both types luminesce with a fluorescence quantum yield of approximately 0.02.[167] The quantum yield of the intercombination transitions into the triplet state B_T is ≤ 0.2 for associated species of type (I) and 0.5 for those of type (II). Under pulsed illumination of deoxygenated solutions, complex associated species of type (I) are capable of a direct transition to the triplet state and in the spectra of such solutions the T–T absorption appears in the red region with $\lambda_{max} = 620$ nm. Fig. 3*a* illustrates the complete $T-T$ absorption spectrum of associated species of type (I). There is a great similarity between this spectrum and the $T-T$ absorption spectrum of rhodamine 6G monomers (fig. 3*b*). The study of the triplet states of associated rhodamine 6G species shows that they are characterised by a number of properties typical for the monomers of the dye: a long lifetime of the triplet state, the occurrence of bimolecular processes involving the deactivation of this state, and electron transfer reactions. The hypothesis of a high reactivity of the triplet states of monomeric molecules can therefore be applied to the triplet states of the associated species.

Measurements of the rate of deactivation of the triplet states of associated rhodamine 6G species showed, firstly, that their formation in solutions leads to an increase of the efficiency of the $T \rightarrow S_0$ intercombination degradation (this is consistent with the hypothesis of the intensification of the spin–orbital interaction in the associated dye), and, secondly, that the lifetime of the triplet states of the associated species is almost independent of the dye concentration, i.e. that the concentration-induced quenching of the triplet states, characteristic of rhodamine 6G monomers[168], hardly takes place with associated species. The latter finding conflicts with the conclusions reached in a study[164] where associated eosin and erythrosin species were investigated at a low temperature.

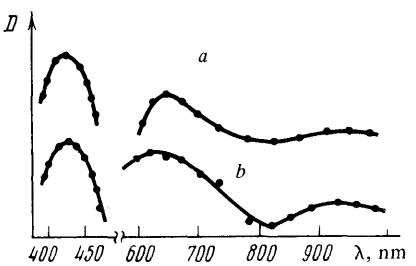


Figure 3. Triplet–triplet absorption spectra: *a*) of associated rhodamine 6G in carbon tetrachloride–butanol mixtures; *b*) of rhodamine 6G monomers in water (at pH 6).

In recent years the photonics of dye molecules have been studied in multicomponent solutions. Investigation of associated derivatives of biphenyl at different temperatures in three-component solutions showed[170] that the radiationless deactivation of their excited singlet state takes place without any appreciable involvement of the triplet level. The intramolecular radiationless deactivation of the fluorescent associated molecules takes place preferentially via the transition to the ground state.

The study of the triplet states and the pathways leading to the deactivation of the electronic excitation energy of associated dye molecules can lead to the elucidation of the causes of the loss of their capacity for luminescence.

VI. ASSOCIATION AND CONCENTRATION-INDUCED QUENCHING OF LUMINESCENCE

The phenomenon of the concentration-induced quenching of luminescence (CQL) consists in the fact that, starting from a threshold concentration of the dye solution, the luminescence yield falls. The concentration-induced quenching of luminescence is usually accompanied by a decrease of the lifetime of the excited state of the dye molecules and by depolarisation of the luminescence. The CQL for solutions of xanthene dyes has been studied quantitatively by Vavilov[171] and Levshin[172-174] and later by Dushinskii[175,176] and Pekerman[177,178]. A characteristic feature of the CQL is a distinct dependence of the nature of the luminescent substances–the CQL has not been observed for many organic compounds over a wide range of concentrations[177].

Physicochemical and physical hypotheses of second-order collisions[171], inductive quenching[179], etc. have been put forward to account for the CQL. Subsequently two approaches to the explanation of the nature of the CQL were outlined. The first is based on the possibility of

† See also A.K.Chibisov and T.D.Slavnova, J.Photochem., 8, 285 (1978).

the inductive resonance migration of the electronic excitation energy between monomeric dye molecules[180]. These ideas subsequently served as a basis of the migration theory of the CQL developed by a number or workers[181-183]. According to this theory, the quenching of the luminescence at high concentrations of the luminescent substances takes place as a result of the resonance transfer of electronic excitation from one dye molecule, in the monomeric form, to another similar molecule. Some of these transitions are accompanied by quenching. However, the cause of the development of radiationless transitions in the migration of excitation has not been specified more precisely. It has been suggested that quenching may occur also in the energy transfer between molecules separated by considerable distances, but the probability of the quenching of excitation in the course of migration increases faster with decrease of the distance than the probability of transfer without quenching. However, there are neither theoretical nor experimental data showing that the fluorescence lifetime and hence the luminescence yield should then decrease. This theory describes quantitatively the changes in the luminescence yield, in the lifetime of the excited state of dye molecules, and in the polarisation of their luminescence as a function of concentration.

Studies of alcoholic solutions of dyes whose electronic absorption spectra do not vary over a wide concentration range but where CQL develops served as an experimental justification of the migration theory of the CQL.[177,178] The absence of concentration-dependent changes in the absorption spectra indicated, according to the authors of the migration theory of the CQL, the absence of physicochemical interactions in solutions, i.e. of the association of dye molecules.

In order to account for the fact that the depolarisation of luminescence occurs appreciably before quenching, it was arbitrarily assumed that there exist two sorts of molecules in solutions: the transfer of excitation to molecules of one sort takes place without quenching, while that to the other involves quenching. The additional hypothesis of the sphere of instantaneous quenching around the excited molecule made it possible[52] to explain the experimental non-parallel concentration variation of the luminescence yield and τ.

Another approach to the explanation of the CQL emphasised the importance of the reversible association of the molecules of luminescent substances. In the first studies on the CQL this phenomenon was accounted for by the inactive absorption of the non-luminescent associated species. A theory of the quenching of luminescence as a result of the migration of excitation energy from monomers to associated species has been developed[184], but in this investigation no account was taken of the inactive absorption by associated species and a number of simplifications were made in the calculations; it was therefore not possible to obtain the correct concentration variation of the effects. The association theory of the CQL created by Levshin[185,186] provides for the intrinsic inactive absorption by the associated species and the migration of excitation from the monomers to these species. The postulates of this theory were subjected to a comprehensive experimental test. Thus, the study of the nature of the CQL in solutions of rhodamines 6G and 3B in various solvents[79,187] made it possible to separate various types of quenching of the luminescence. The associative nature of the CQL in aqueous and glycerol solutions of Na-fluorescein has been demonstrated[61]. In these and in a number of other studies[60,109] it was shown that, even if the migration of the electronic excitation between monomeric molecules does lead to radiationless processes in the latter, this plays a very insignificant role in the overall CQL.

The study of concentration effects in alcoholic solutions of rhodamine dyes[16], whose absorption spectra do not change appreciably even in the case of concentrated solutions, showed that the CQL observed in such spectra if related to the association of the dye molecules. This was established by measuring the number-average molecular weight. Fig. 4 presents the concentration variation of the luminescence yield (curve *1*) and of the relative number-average molecular weight of rhodamine 6G (curve *2*) in ethanol. The resolution of the CQL into migration quenching (curve *3*) and quenching due to the inactive absorption by associated species (curve *4*) showed that the variation of the migration quenching of luminescence and of τ with concentration is the same. This demonstrates that the discrepancy between the variation of the yield and τ with concentration is associated with the inactive absorption by the associated species and that the so-called sphere of instaneous quenching does not exist.

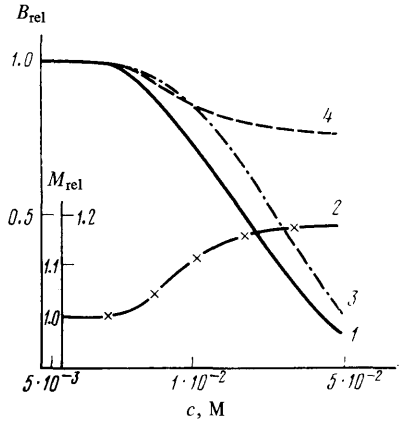


Figure 4. Dependence of the luminescence yield (curve *1*) and the number-average molecular weight (curve *2*) of rhodamine 6G in ethanol on concentration; 3) quenching due to the migration of energy; 4) quenching consequent upon the inactive absorption by the associated species.

Measurement of the differential spectra of alcoholic solutions of rhodamine dyes[188] also showed that associated species are formed at high concentrations.

In recent years both theoretical and experimental problems of the CQL in solutions of organic dyes have been considered by Bojarski and coworkers and other investigators[189-193], who based their treatment on association hypotheses. They take into account the possibility of multistage excitation energy transfer to associated species, involving several molecules, as a result of which the electronic excitation energy is converted into heat[194]. This more general theory of the CQL leads to the following dependence of the relative luminescence quantum yield B on concentration:

$$B/B_0 = [1 - f(\gamma)]/[1 - \alpha f(\gamma)], \quad (32)$$

where

$$f(\gamma) = \pi^{1/2}\gamma e^{\gamma^2}\left[1 - 2\pi^{-\frac{1}{2}}\int_0^{\gamma} e^{-t^2}dt\right],$$

$$\gamma = \gamma_м + \gamma_a = (c_м/c_{0м} + c_a/c_{0a})(\pi B_0)^{1/2}/2,$$

$$\alpha = \gamma_м/(\gamma_м + \gamma_a),$$

c_m and c_a are the concentrations of the monomers and associated species, c_{0m} and c_{0a} are the critical concentrations for the radiationless excitation energy transfer between monomers and between monomers and associated species, and B_0 is the luminescence quantum yield for the dye solution in the absence of quenching. For $\gamma_m \ll \gamma_a$, this expression becomes identical with that obtained by Förster[195]. An experimental test carried out on aqueous and aqueous glycerol solutions of xanthene dyes[191], including the anti-Stokes region[196], indicated a satisfactory agreement with theory. The parameter taking into account the quenching of the luminescence in the transfer of electronic excitation between monomers then has a value such that the above process hardly leads to CQL. It has been shown theoretically[197] that, in the dipole–dipole interaction between luminescent molecules, there is a change in the angular dependence of the probability of the absorption and emission of light with increase of their concentration. In the migration theory of the CQL [52] this change is taken into account with the aid of the hypothesis of an instantaneous transfer. An estimate[197] of the size of the "sphere of instantaneous transfer" showed that the angular effect can influence the anisotropy of the emission only in the presence of associated species in solution.

Thus theoretical and experimental studies fully confirm that the concentration-induced quenching of luminescence in solutions of organic dyes involves the formation of associated molecules in the latter.

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Kinetics and Catalysis of the Oxidation of Titanium, Silicon, Germanium, and Gallium Arsenide

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A systematic account is given of the results of studies of the kinetics and catalysis of thermal gas-phase oxidation reactions of titanium, silicon, germanium, and GaAs. The influence of various factors (the nature of the reactant gas, the method of the preliminary treatment of the surface, and the nature of the substance oxidised) on the reaction kinetics has been estimated. The characteristics of the catalysis of heterogeneous oxidative processes are discussed and new ways of solving a number of practical problems are outlined.
The bibliography includes 133 references.

CONTENTS

I. Introduction 1092
II. Thermodynamics of the oxidation of titanium, silicon, germanium, and gallium arsenide 1092
III. Kinetics and mechanism of the oxidation of metals and semiconductors 1093
IV. Catalysis of the oxidation of titanium, silicon, germanium, and gallium arsenide 1099
V. Some practical applications 1104

I. INTRODUCTION

The development of microelectronics, radio engineering, and laser and space technology has necessitated intense research into the characteristics of the chemical interaction of metals, alloys, and semiconductors with other elements and also a more detailed investigation of the structure of solids and of solid-state reactions.

Reactions involving the thermal oxidation of titanium, silicon, germanium, and gallium arsenide are technological processes in the radio engineering and semi-conductor industry. In order to obtain oxide films with specified properties, it is important to investigate the thermodynamics, kinetics, and mechanisms of these reactions. In the development of modern electronic engineering it is urgently necessary to accelerate the growing of oxide layers. Heterogeneous catalysis plays an important role in the solution of such problems.

However, despite the abundance of experimental data[1-14], many problems of the kinetics and catalysis of heterogeneous Ti, Si, Ge, and GaAs oxidation reactions have been by no means adequately investigated. The use of catalysis in the technology for the preparation of oxide films is hindered by the fact that the mechanism and nature of the catalytic acceleration of the reaction have not been ultimately elucidated and the selection and preparation of the catalyst presents certain difficulties[15-18].

The present review surveys the results of studies on the kinetics and catalysis of the high-temperature gas-phase oxidation of titanium, silicon, germanium, and gallium arsenide and describes practical ways of employing heterogeneous catalysis in technology.

II. THERMODYNAMICS OF THE OXIDATION OF TITANIUM, SILICON, GERMANIUM, AND GALLIUM ARSENIDE

In the thermal oxidation of metals and semiconductors there is a decrease of the free energy ΔG°_{T}. Analysis of the thermodynamics of titanium oxidation reactions in various gaseous media (in air, water vapour, and carbon dioxide) in the temperature range 400-1000°C and of the interactions of silicon, germanium, and gallium arsenide with oxygen showed that the most probable products of the interaction are crystalline or vitreous TiO_2, SiO_2, GeO_2, and Ga_2O_3 films[1,2,6,9-11,19-27]. Reactions (1)-(7), occurring under these conditions, are virtually irreversible[29,30]:

$$Ti(solid) + O_2(gas) = TiO_2(solid), \quad (1)$$

$$Ti(solid) + 2H_2O(gas) = TiO_2(solid) + 2H_2(gas), \quad (2)$$

$$Ti(solid) + 2CO_2(gas) = TiO_2(solid) + 2CO(gas), \quad (3)$$

$$Si(solid) + O_2(gas) = SiO_2(solid), \quad (4)$$

$$Ge(solid) + O_2(gas) = GeO_2(solid), \quad (5)$$

$$2GaAs(solid) + \tfrac{3}{2}O_2(gas) = Ga_2O_3(solid) + As_2(gas), \quad (6)$$

$$2GaAs(solid) + \tfrac{3}{2}O_2(gas) = Ga_2O_3(solid) + \tfrac{1}{2}As_4(gas). \quad (7)$$

The results of the calculations of the principal thermodynamic characteristics of reactions (1)-(7) using literature data[28] are presented in Tables 1 and 2. Table 1 shows that a high negative standard Gibbs free energy and highly exothermic heats are characteristic of reactions (1)-(3), which indicates their virtual irreversibility[30].

The thermodynamic probability of the oxidation of silicon, germanium, and gallium arsenide via the reactions[11,31,32]

$$Si(solid) + \tfrac{1}{2}O_2(gas) = SiO(gas),$$
$$Ge(solid) + GeO_2(solid) = 2GeO(gas),$$
$$2GaAs(solid) + \tfrac{1}{2}O_2(gas) = Ga_2O(gas) + As_2(gas).$$

increases with increase of temperature to 1000-1300°C. The equilibrium GeO vapour pressure is significant (approximately 10^{-5} atm) already above 600°C. The partial pressures of SiO and Ga_2O are negligible even at approximately 1300°C and oxygen pressures up to 10^{-9} atm.[11]

The oxidation of gallium arsenide involves the formation of gaseous arsenic in the form of As_2 and As_4.[11,33-37] Under these conditions, the presence of As_4 molecules in

the gas phase is thermodynamically more probable (see Table 2).

Table 1. Temperature variation of ΔH°_T, ΔS°_T, ΔG°_T, and $\lg K_p$ for the thermal oxidation of titanium [reactions (1) to (3)]. [130]

T, °C	ΔH°_T, kcal mole^{-1}	ΔS°_T, cal mole^{-1} K^{-1}	ΔG°_T, kcal mole^{-1}	$\lg K_p$
		Reaction (1)		
400	−224.988	−42.74	−196.224	63.73
500	−224.742	−42.40	−191.967	54.28
600	−224.511	−42.12	−187.741	47.01
700	−224.302	−41.89	−183.543	41.23
		Reaction (2)		
400	−107.762	−17.93	−95.695	31.08
500	−107.130	−17.05	−93.951	26.57
600	−106.535	−16.31	−92.296	23.11
700	−105.984	−15.72	−90.689	20.37
		Reaction (3)		
400	−90.159	−2.08	−88.760	28.82
500	−90.258	−2.21	−88.550	25.04
600	−90.440	−2.44	−88.310	22.11
700	−90.705	−2.73	−88.049	19.78

Table 2. Temperature dependence of $\lg K_p$ for the thermal oxidation of silicon, germanium, and gallium arsenide [reactions (1)–(7)]. [133]

No. of reaction	$\lg K_p$			
	400°	500°	600°	700°
(4)	61.23	52.44	45.22	39.65
(5)	35.88	30.32	26.06	22.53
(6)	1.41	1.80	2.18	2.54
(7)	60.51	52.23	45.99	40.96

III. KINETICS AND MECHANISM OF THE OXIDATION OF METALS AND SEMICONDUCTORS

The rate of formation of thin films in the oxidation of metals and semiconductors are described by different equations depending on the temperature and the reaction time; it can obey the following laws[9,11,12,38–42]:

(1) A direct logarithmic relation:

$$y = k_1 \lg(B\tau + 1);$$

(2) An inverse logarithmic relation:

$$k_2/y = A + \lg \tau;$$

(3) A linear relation:

$$y = k_3\tau;$$

(4) A parabolic relation:

$$y^2 = k_4\tau;$$

(5) A cubic relation:

$$y^3 = k_5\tau,$$

where y is the thickness of the oxide film, τ the time, and A, B, and k_1–k_5 are constants. For thin films, logarithmic and cubic relations for their thickness as a function of time predominate, while for thick films the parabolic and linear relations predominate[43].

The study of the kinetics of the oxidation of titanium, silicon, germanium, and gallium arsenide led to the discovery of relations of three types[11,39]: linear, logarithmic, and parabolic (Fig. 1).

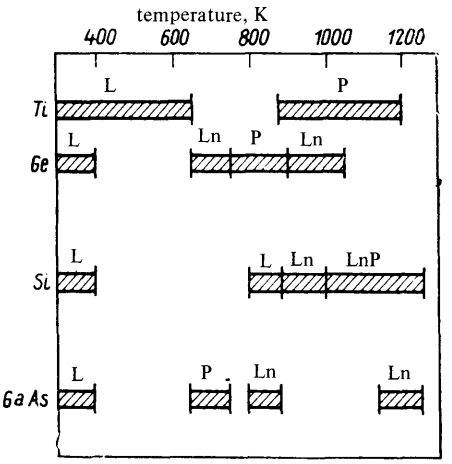


Figure 1. Dependence of the type of kinetic relation for the oxidation of titanium, silicon, germanium, and gallium arsenide on the process temperature: L = logarithmic relation; Ln = linear relation; P = parabolic relation; LnP = linear-parabolic relation.

Despite the satisfactory agreement between the experimental rates of oxidation, phase composition of the product, and other process parameters obtained by different workers, the treatment of the experimental results and of the oxidation mechanisms were different in different investigations[1,7,8,38,43–57]. Wagner[49,50] justifies a parabolic law governing the rate of growth. He postulates that, at comparatively high temperatures and for fairly high film thicknesses, the oxidation process takes place as a result of the diffusion of ions and electrons through the growing oxide; it is assumed that each volume element of the oxide is electrically neutral. The theory of Mott and Cabrera[51] explains the inverse logarithmic and parabolic variation of the rate of growth for comparatively thin films taking into account the influence of the electric field on the diffusion of ions in the oxide. However, Kubaschewski and Hopkins[43] believe that the films obtained in the oxidation of titanium at 300–500°C are somewhat thicker than should have been the case if their growth can be accounted for by the transport of material under the influence of the electric field. They begin with the hypothesis that microcavities are formed on the metal–oxide interface, i.e. they adopt the Evans theory[58], according to which the rate of formation of oxide films is determined by the transport of ions through a thin oxide film. The theory of Mott and Cabrera was subsequently developed by Hauffe and Ilschner[52], who explained the direct logarithmic relation for the rate of growth of the oxide film in the initial stages of the oxidation of metals and semiconductors.

A general model has been proposed for the mechanism of the growth of oxide films[53,54]. It is based on the treatment of processes involving the diffusion of ions and electrons through the oxide layer in which an electric field

created by these diffusing species operates. The difference between the proposed oxidation mechanism and those existing previously consists in the fact that, instead of one equation for the description of the diffusion of ions and electrons, two such equations are used in calculations of the rate of diffusion. This makes it possible (by combining the equations for total electric field) to simplify the description of the rate of growth of the oxide film thickness. However, the model suffers from the disadvantage that it does not take into account the transport process in the gas phase, the adsorption of oxidant on the surface of the oxide, and certain other factors[11].

The problem of the nature of diffusing species of oxidation remains controversial. Thus it has been shown[55] that an electric field at right angles to the outside film can accelerate or retard the oxidation of silicon, showing that the reaction takes place as a result of the transfer of ions through the oxide film. It has been established[56] that neutral oxygen atoms diffuse in addition to ions.

The rate of oxidation of gallium arsenide at comparatively low temperatures is controlled by diffusion through the oxide layer and at higher temperatures by the intrinsic chemical reaction between oxygen and gallium arsenide on the reaction interface[57]. This has been confirmed in studies[33,61] where the oxidation of GaAs was studied in oxygen at 600–900° C. It was established that the rate of oxidation below 600° C is insignificant, while on heating above 900° C the rate is so high that the oxidised specimen burns.

Thus the survey of literature data on the oxidation of titanium, silicon, germanium, and gallium arsenide shows that many problems of the kinetics and mechanisms for these chemical reactions are still unsolved. It is therefore of interest to investigate the influence of different factors on the oxidation kinetics: (a) the nature of the reactant gas; (b) the preliminary treatment of the metal surface; (c) the chemical composition of the alloy.

1. KINETICS AND MECHANISM OF THE OXIDATION OF TITANIUM IN AIR; IN WATER VAPOUR, AND IN CARBON DIOXIDE

The kinetics of the oxidation of titanium in various gaseous media have been little investigated at present as a function of temperature and the duration of heating of the metal. The oxidation of titanium is an extremely complex process, because, in contrast to other metals, the oxidation of titanium and its alloys leads to the formation of gas-saturated layers consisting of solid solutions of oxygen in α-titanium in addition to oxide films or scale.

Jenkins[62], who investigated the kinetics of the saturation of titanium with oxygen over a wide range of temperature, proposed a diagram illustrating the nature of the oxidation of titanium (Fig. 2). The diagram is divided into three main regions: *A*, *B*, and *C*. Region *A* characterises the oxidation at high temperatures in accordance with the parabolic law, which involves the simultaneous occurrence of two processes—the dissolution of oxygen and the formation of the oxide layer. The oxide grains are larger and better formed than at low temperature. Two-sided diffusion of oxygen and titanium through dense oxide layers takes place under these conditions. Region *B* corresponds to the oxidation of titanium at moderate temperatures where oxygen is absorbed via a parabolic law in the first stage and then, when the oxide thickness reaches a critical value, the latter is replaced by a linear law. The linear relation reflects mainly the growth of the oxide film, while the dissolution of oxygen continues at a rate determined by the oxygen concentration gradient and the diffusion coefficient of oxygen in the metal. The oxide lacks an appreciable protective capacity and has a porous structure, which facilitates the penetration of gaseous oxygen to the interface between the oxide and the metal. Region *C*, which characterises the oxidation of titanium at low temperatures, corresponds to a logarithmic law for the absorption of oxygen by titanium. Thus the difference between the types of kinetic curves is not associated solely with the temperature factor. The nature and mechanism of the oxidation and different stoichiometric compositions and crystal structures of the oxides formed on the metal surface play the main role.

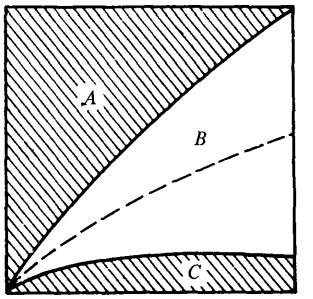


Figure 2. Titanium oxidation diagram: A) at high temperatures; B) at moderate temperatures; C) at low temperatures (V is the total amount of absorbed oxygen).

The interaction of metals with gases is due to diffusion and can be represented by three main stages[59]: (1) the adsorption of the gas on the metal surface; (2) the initiation of a crystal of the new compounds; (3) crystal growth. At a certain stage of the adsorption process, where the gas does not dissolve in the metal, a second type of crystal lattice arises on the surface of the metal instead of the single type of lattice of the main metal as a result of the solid-phase reaction. The interface then consists of two coherently bound crystalline layers—the metal and the oxide. The formation of the lattice of the new compound on the surface of the metal obeys the principles of orientation and dimensional correspondence[60].

(a) Interference Films on Titanium

The oxidation of metals by atmospheric oxygen or other oxidants results in the formation on their surface of oxide films whose thickness may vary within very wide limits. It is usual to distinguish three types of films: thin (from several angstroms to 200–400 Å), medium (from 400 to 5000–10 000 Å), and thick (above 5000–10 000 Å)[40,63–66]. For a thickness exceeding 200–400 Å, the films begin to acquire a colour due to the interference of light (interference colours)[38,42,43,64]. The phenomenon of the interference colours of films on metals has been studied fairly widely, particularly for elements such as iron, nickel, copper, silicon, and germanium[67–74]. However, despite

the abundance of the literature on the oxidation of titanium, the formation and properties of interference films on this metal have not been widely described in the scientific literature and are considered in only one monograph[1] devoted to the oxidation of titanium and its alloys.

This presents[1] the colours of four orders of spectra but the question of the number of spectra remained open. In order to study this problem in greater detail, the colour spectra of oxide films on iodide titanium (~99.90% Ti), technically pure VT-1 titanium (≥99.5% Ti), and OT4-0 (≥96.5% Ti) and OT4-1 (≥95% Ti) alloys were investigated[130] between 500° and 800°C.[17,21,22,25,73,130] At 500°C the oxidation is comparatively slow; a long time is required even for the completion of the formation of films giving the first-order spectrum. At 700° and 800°C there is a rapid growth of oxide films and at higher temperatures continuous observation of the change of the colour of the film is difficult owing to the high rate of oxidation and heating of the metal to a red glow, which masks the colour. At these temperatures the colour of the film can be more conveniently determined by quenching the specimens. For example, blue films (in a first-order spectrum) on specimens of the OT4-0 alloy are formed at 500°, 600°, 700° and 800°C respectively after 6000, 342, 70 and 30 s.

A temperature of 600°C, at which there is a smooth transition from one colour to another, made it possible to observe and record the alternation of five interference colour spectra on iodide and technically pure titanium and the OT4-0 titanium alloy and four such spectra on the OT4-1 alloy. Comparison of the times required to complete the first-order spectrum at 600°C showed that the oxidation proceeds at the highest rate on the VT-1 alloy (80 s) and at the lowest rate on the OT4-1 alloy (460 s). With increase of the thickness of the coloured film, the oxidation process slows down (Table 3).

Table 3. The formation of interference films with a first-order spectrum on titanium and its alloys in oxidation in air at 600°C.[130]

Colour of film	Oxidation time of specimens, s		
	VT-1	iodide titanium	OT4-0
Pale yellow	8	18	30
Yellow	13	27	39
Brown	22	37	60
Violet	26	55	85
Dark blue	35	123	169
Blue	49	330	342
Pale blue	80	367	390

The mechanism of the formation of thin oxide films on metals, proposed by Mott and Cabrera, presupposes the generation of an electric field in such films[38,42,51,52,69,76-78] whose potential gradient reaches approximately 10^7 V cm^{-1}. Under the influence of such films, the metal cations acquire a high mobility and migrate at a high rate through the film towards its boundary with the gas, which leads to a fairly rapid growth of the film on the metal surface. With increase of film thickness, the potential gradient diminishes significantly and the oxidation slows down.

We shall apply this oxidation mechanism to metals which give rise to semiconducting *p*-type films with an excess of cationic vacancies[43]. The applicability of this theory to the explanation of the oxidation of titanium is apparently somewhat limited for the following reasons: (1) titanium gives rise to the oxide TiO_2, which is an *n*-type semiconductor (with a deficiency of anions)[43]; (2) titanium is characterised by unusually high solubility of oxygen, which penetrates into the bulk of the metal[5,6,19,43]; (3) a film, whose thickness amounts to hundredths of angstroms within the limits of the operation of the logarithmic law, grows on titanium[1,79].

In our view extensive study of the properties of interference films on titanium and its alloys can yield valuable information about the kinetics, catalysis, thermodynamics, and physicochemical properties of the oxide layers formed and about the mechanism of the interaction of metals with the medium.

(b) Oxidation in Air

Studies on the kinetics of the oxidation of titanium in air are particularly important. Their results are presented in numerous publications[1,8,39,44-48], where it is shown that appreciable differences in the nature of the oxidation of titanium in oxygen and in air are not observed during the initial period[1,8]. In the oxidation by air, the shape of the kinetic curves and the form of the kinetic relation are analogous to those obtained in the oxidation of titanium in pure oxygen (700–1000°C), but the degree of oxidation is lower than in oxygen[1,8]. The rutile lattice constants in the oxides obtained by oxidising titanium in air and in oxygen are the same at temperatures below 1100°C.[8]

Subsequently (at higher temperatures) titanium absorbs a much greater amount of gases in oxidation in air than in oxidation in oxygen. Above 1150°C the oxidation of titanium in air is faster than in oxygen[80]. The process is complicated by the fact that, in the high-temperature oxidation of titanium in air, the metal reacts not only with oxygen but also with nitrogen. It has been established[59,80] that nitrogen enters the crystal lattice of rutile in the course of the high-temperature oxidation with air, which leads to the formation of a perforated structure and an increase of the volume of the unit cell. The formation of rutile with a defective lattice facilitates the diffusion of titanium ions to the outer surface of the oxide layer and the diffusion of oxygen into the bulk of this layer, which promotes a more rapid oxidation. At the same time, there is no unanimous view in the literature concerning the rate of oxidation of titanium in oxygen and in air. Apart from the data quoted above, it has also been claimed[81,82] that the oxidation of titanium at 1200°C in pure oxygen is much faster than in air and that the rate of oxidation is virtually the same in the two cases at 1000°C.

Studies of the initial stages of the oxidation of titanium are particularly difficult in view of the difficulty of measuring the thickness of the oxide layer and the amount of substances which have reacted in the course of the high-temperature chemical interaction. The method of interference indicators has been used in studies of the kinetics of the initial stages of the oxidation of titanium[17]. The rate of oxidation was found by observing the interference of the light waves in oxide films of specified thickness, formed as a result of the heterogeneous chemical interaction of the metal with the oxidising medium. The main advantage of this method is that one has only to determine the colour of the oxide and not its thickness. The method of interference indicators permits comparative kinetic studies and enables one to determine the influence of the chemical composition of titanium alloys on the initial stages of their oxidation[22,29,75,83-85], the difference between the

rates of reaction in air[17,29,84,85], water vapour[24,29,84–86], and carbon dioxide[24,29,84,85,87], the influence of catalysts on the process kinetics[88–92], and the dependence of the kinetics of the initial stages of the oxidation of titanium on the method of polishing of the metal surface[23,93,94] and other factors.

Table 4. Chemical composition of titanium alloys[22].

Alloy	Concentrations of components, wt.%						
	Ti	Al	Mn	Fe	Si	C	others
VT-1	99.5	—	—	—	—	—	—
OT4-0	⩾96	0.2–1.4	0.2–1.3	⩽0.3	⩽0.15	⩽0.1	⩽0.8
OT4-1	⩾95	1.2–2.5	0.7–2.0	⩽0.3	⩽0.15	⩽0.1	⩽0.8

A comparative study of the kinetics of the growth of interference oxide layers in the thermal oxidation in air of specimens of technically pure titanium of type VT-1 and of OT4-0 and OT4-1 titanium alloys has been carried out[17,29,84,85] (Table 4). Metal specimens with dimensions 20 × 10 × 1 mm were subjected to isothermal oxidation at 500–650°C in a furnace with transparent quartz inspection windows for the visual observation of the changes in the colour of the film during the reaction.

Table 5. The colours of titanium oxide films as a function of the thickness of the oxide layer[1].

Colour of film	y, Å
Pale yellow	344
Yellow	349
Brown	447
Violet	492
Dark blue	515
Blue	536
Pale blue	542

Table 6. The activation energies (E, kcal mole^{-1}) for the oxidation of titanium alloys by air with formation of interference films having a first-order spectrum[22,23].

Alloy	Change in film colour		
	from yellow to brown	from brown to violet	from violet to dark blue
VT-1	15.700	23.000	28.800
OT4-0	24.400	26.800	29.000
OT4-1	26.200	27.000	39.200

The relations between the colour of the first-order spectrum and the thickness of the oxide film on titanium are presented in Table 5 for interference films. Experiments at different temperatures led to the determination of the time corresponding to the change in the colour of the oxide film within the limits of two chosen colours–from yellow to brown (Δy = 98 Å), from brown to violet (Δy = 45 Å), from violet to dark blue (Δy = 23 Å), and from dark blue to blue (Δy = 21 Å). The experimental results were expressed by plots of $\tau = \varphi(t^0)$ and $\lg \tau = \varphi(1/T)$. Fig. 3 illustrates the kinetics of the oxidation of titanium alloys by air accompanied by a change in the colour of the film from yellow to brown[84]. Table 6 presents the activation energies for the oxidation of titanium alloys in air found from plots of $\lg \tau = \varphi(1/T)$.

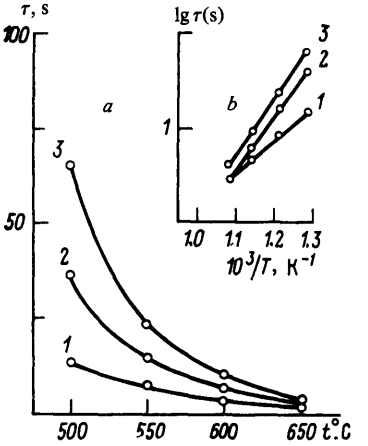


Figure 3. The film formation time τ in the yellow–brown colour range as a function of temperature t(°C) (*a*) and $1/T$ (*b*) in the oxidation of titanium alloys by air; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

(c) Oxidation in Water Vapour and Carbon Dioxide

In order to elucidate the influence of the nature of the oxidising medium on the rate of oxidation of titanium and its alloys, a study was made of the kinetics of the initial stages of the oxidation of the metal in water vapour and carbon dioxide under the conditions of the formation of an interference film with a first-order spectrum[24,29,84–87].

The kinetics of the oxidation of titanium in water vapour have been studied comparatively little. This problem has been described most completely in a monograph[1] and in a number of papers[95–97]. The studies showed that at a water vapour pressure of 1 atm and at 400–1200°C the oxide films grow faster than in air owing to the looser structure of the layer of scale. At 800–1000°C the thickness of the film increases in accordance with the same laws as in air[1].

The study[24,29,84–87] of the initial stages of the oxidation of titanium alloys in water vapour and carbon dioxide and comparison of the results with the oxidation kinetics in air showed that the nature of the oxidising medium has a significant influence on the rate of growth of the interference films. In the presence of water vapour the formation of a film having a standard colour is much faster on all three alloys in the range of experimental temperatures than in air and in carbon dioxide (Fig. 4).[24] For example, the change in the colour of the film from yellow to brown on specimens of the OT4-0 alloy at 550°C in water vapour,

air, and carbon dioxide takes place after 22, 230 and 287 s respectively. The apparent activation energies for the oxidation of titanium alloys in water vapour and carbon dioxide are presented in Table 7.

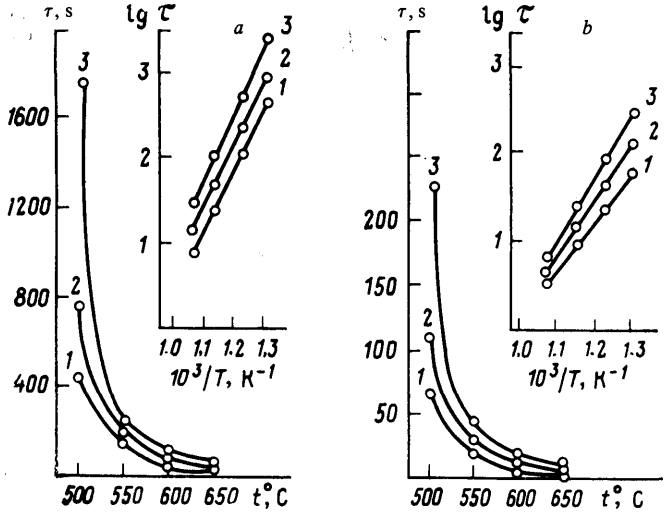


Figure 4. Dependence of the oxidation time τ of mechanically polished titanium alloy specimens on temperature in the formation of the film in the colour range from violet to dark blue: *a*) in carbon dioxide; *b*) in water vapour; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

Table 7. The activation energies (E, kcal mole^{-1}) for the oxidation of mechanically polished titanium alloy specimens in water vapour and carbon dioxide[24,29].

Alloy	Change in film colour			
	from yellow to brown	from brown to violet	from violet to dark blue	from dark blue to blue
	in water vapour			
VT-1	21.200	24.900	29.400	35.800
OT4-0	24.400	27.000	32.400	38.300
OT4-1	26.600	28.000	35.800	40.900
	in carbon dioxide			
VT-1	30.500	34.800	39.100	40.000
OT4-0	31.400	36.600	40.500	41.800
OT4-1	31.700	37.400	41.800	42.900

It follows from the analysis of the data presented in Tables 6 and 7 and in Figs. 3 and 4 that, in the formation of an oxide layer in air, water vapour, and carbon dioxide, technically pure VT-1 titanium is oxidised at the highest rate in all the intervals of the first-order colour spectrum investigated, while the lowest rate corresponds to the OT4-1 alloy with the highest aluminium content. According to some investigations[1,8,43], alloying with aluminium greatly increases the heat resistance of titanium alloys. The highest activation energies for the oxidation reaction correspond to specimens of the OT4-1 alloy under these conditions.

The retardation of the interaction of the metal with the medium as the thickness of the oxide layer (Figs. 5 and 6) increases and the increase of the activation energy for the process are characteristic of all three alloys. This can be explained by the fact that the oxide layer formed on the metal exhibits more effective protective properties and, by separating the reactants, strongly inhibits the chemical interaction and weakens the effect of the electric field arising on formation of interference oxide layers on metals[38,42,69].

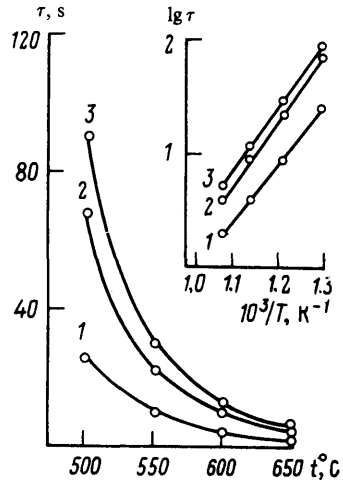


Figure 5. Dependence of the coloured film formation time in the oxidation of electrochemically polished titanium alloy specimens in water vapour on temperature in the colour range from yellow to brown; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

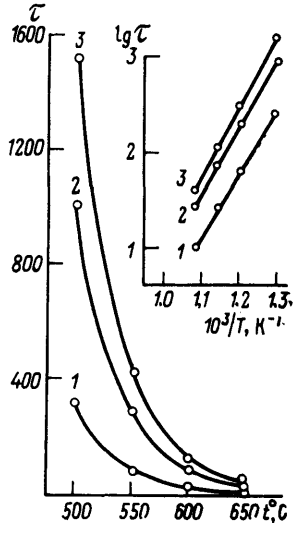


Figure 6. Dependence of the coloured film formation time in the oxidation of electrochemically polished titanium alloy specimens in carbon dioxide on temperature in the colour range from yellow to brown; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

An electron diffraction study of the phase composition of the interference films[98,99] formed in the thermal oxidation of titanium alloys in water vapour showed that the principal structural component of the films is rutile. The films obtained by oxidising the metal in CO_2 include three structural components: rutile, anatase, and titanium carbide[24,29].

The increase of the rate of oxidation of titanium in water vapour is due to the more porous structure of the oxide layer and the increase in the number of defects in the crystal lattice of rutile (an excess of titanium ions), which has been confirmed by electron microscope studies and is consistent with other data[95–97]. Under these conditions, there is a marked increase of the diffusional mobility of titanium ions. The diffusion coefficient of titanium ions in the oxide layer obtained in water vapour exceeds by 1–2 orders of magnitude that in the oxide obtained in air[1].

The decrease of the rates of the initial stages of the oxidation of the alloys during the formation of interference films with a first-order spectrum, in carbon dioxide is apparently associated with the formation of titanium carbide (a phase with a very great hardness and density in which the rate of diffusion of titanium ions is correspondingly reduced) in the surface layer of the metal. This is also indicated by the higher activation energy for the oxidation of titanium alloys in a stream of CO_2 compared with air and water vapour[24,29].

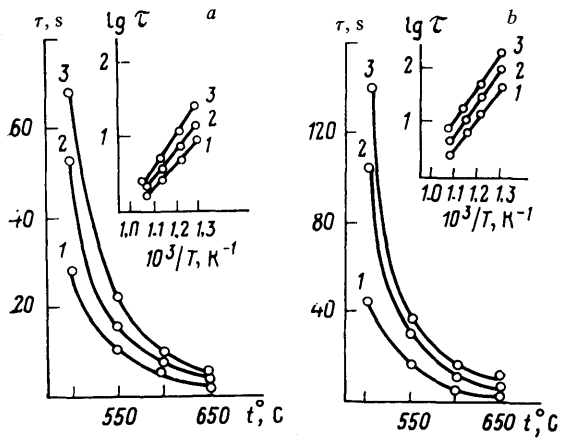


Figure 7. Dependence of the oxidation time for mechanically (*a*) and electrochemically (*b*) polished titanium alloy specimens on temperature (°C) in the formation of the film in water vapour in the colour range from brown to violet: *a*) water vapour; *b*) carbon dioxide; alloy: *1*) VT-1; *2*) OT4-0; *3*) OT4-1.

(d) The influence of the Method of Polishing the Surface on the Kinetics of the Oxidation of Titanium Alloys

The method of polishing the metal surface has an appreciable influence on its properties. For example, in electrochemical polishing the microgeometry and the physical and chemical properties of the surface are altered[100]. The method of preparation of the metal surface influences the kinetics of the initial stages of its oxidation[40]. However, the determination of the differences between the rates of oxidation of the surfaces of specimens of the metal having the same composition and structure but subjected to different types of treatment is experimentally difficult. The method of interference indication[17], which in the given instance is extremely sensitive and very promising, has been used to solve this problem.

In order to investigate the influence of the method of treatment of the surfaces of titanium alloys on the kinetics of their oxidation in different gaseous media, specimens of technically pure VT-1 titanium and OT4-0 and OT4-1 titanium alloys were subjected to two types of polishing: mechanical polishing to give a roughness of class 10–12 and electrochemical polishing in an electrolyte solution: the composition of the electrolyte and the process conditions have been described[101–103]. It has been shown that in the gaseous media investigated the initial stages of the oxidation of titanium specimens subjected to electrochemical polishing in the course of the formation of colour films with a first-order spectrum are much slower compared with specimens subjected to mechanical polishing (Fig. 7).[94] For example, the change in the colour of the film from violet to dark blue on mechanically polished specimens of the OT4-1 alloy at 550°C in water vapour, air, and carbon dioxide takes place after 45, 116, and 210 s, while on electrochemically polished specimens the corresponding times are 80, 660, and 756 s respectively.

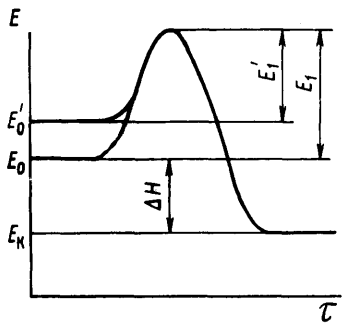


Figure 8. Variation of the energy levels of the surface atoms in the polishing process; E is the activation energy, τ is the time, E_0 and E_0' are the initial energy of the atoms in the surface layer for the electrochemically and mechanically polished specimens respectively, E_1 and E_1' are the activation energies for their oxidation, ΔH is the heat of the chemical reaction, and E_e is the energy of the reaction products.

The appreciable difference between the rates of the initial stages of the oxidation reaction can be explained by the fact that the energy levels of the atoms in the surface layer are higher for a mechanically polished (cold-worked) surface than for an electrochemically polished surface (Fig. 8).[94] The cold-worked layer, usually concentrated in the surface region, is removed by electrochemical polishing[104,105]. Furthermore, after electrochemical polishing one observes an increased resistance to gaseous corrosion due to the presence of a continuous thin and stable

oxide film on the surface of the metal[104,106–108]. On the other hand, in the case of mechanical polishing the scratches and foreign inclusions on the surface prevent the creation of such a continuous oxide layer and oxidation proceeds at a higher rate. With increase of the thickness of the coloured films, the rates of oxidation of both mechanically and electrochemically polished specimens of titanium alloys decrease in air, water vapour, and carbon dioxide.

Table 8 presents as an example the activation energies for oxidation in water vapour for specimens subjected to electrochemical polishing. Comparison of the data in Tables 6–8 shows that the activation energies for the oxidation of electrochemically polished titanium alloy specimens are appreciably higher than for mechanically polished specimens.

Table 8. The activation energies (E, kcal mole^{-1}) for the oxidation of electrochemically polished titanium alloy specimens by water vapour[84,94].

Alloy	Change in film colour			
	from yellow to brown	from brown to violet	from violet to dark blue	from dark blue to blue
VT-1	23.900	25.600	32.200	38.500
OT4-0	26.800	28.800	34.200	40.200
OT4-1	27.500	29.700	36.400	41.700

Regardless of the method of preliminary treatment of the surface, among the three alloys investigated technically pure VT-1 titanium and the OT4-1 alloys are oxidised at the highest and lowest rates respectively. Correspondingly, higher activation energies are characteristic of OT4-1 alloy specimens than of the VT-1 titanium.

Thus the method of interference indicators made it possible to observe the influence of the method of polishing the surface on the kinetics of the oxidation of titanium alloys of different composition in different gaseous media.

2. KINETICS OF THE OXIDATION OF GERMANIUM AND GALLIUM ARSENIDE

The kinetics of the thermal oxidation of germanium in air have been investigated[90,91,109,110] in the temperature 575–625°C in the region of the colour change at the GeO_2 film from colourless to green; with increase of the thickness of GeO_2 layers, an appreciable increase of the activation energy for the process is observed—from 47 to 128 kcal mole^{-1}.

Mathematical treatment of the results of the experiment on the oxidation of GaAs plates of AGET brand with atmospheric oxygen yielded[133] the following relations between the oxidation time τ and the temperature T in the range 600–675°C in different oxide colour ranges:

from colourless to brown:

$$\tau \simeq 52.48 \cdot 10^{-7} \exp(9950/T);$$

from brown to violet:

$$\tau \simeq 32.62 \cdot 10^{-17} \exp(33080/T);$$

from violet to dark blue:

$$\tau \simeq 12.59 \cdot 10^{-21} \exp(42300/T);$$

from dark blue to blue:

$$\tau \simeq 31.62 \cdot 10^{-24} \exp(47900/T).$$

It was shown that the activation energy for the formation of the β-Ga_2O_3 oxide film on the gallium arsenide specimens increases with increasing thickness of the oxide, within the limits of the first interference colour spectrum, from 19.81 to 95.32 kcal mole^{-1}.[133] This finding has been explained in a number of studies[11,42,77,78].

IV. CATALYSIS OF THE OXIDATION OF TITANIUM, SILICON, GERMANIUM, AND GALLIUM ARSENIDE

It is known that, in selecting catalysts for a given reaction, it is necessary to choose the latter from substances which are known as catalysts of analogous reactions and which form with initial reactants and the reduction products compounds which can be readily decomposed[111–115]. For titanium, silicon, germanium, and gallium arsenide heterogeneous oxidation processes, the optimum catalysts employed were therefore platinum, palladium, and silver, which are traditional catalysts of a large class of oxidation reactions[116].

1. METHODS OF PREPARATION OF THE CATALYSTS

The platinum, palladium, and silver catalysts have been obtained by electrolysing 3% aqueous solutions of chloroplatinic acid, palladium chloride, and potassium silver cyanide respectively. The carriers were platinum, silver, and nichrome. In addition, the platinum catalyst has been obtained by the thermal decomposition of $H_2[PtCl_6]$. For this purpose, a 50% aqueous solution of $H_2[PtCl_6]$ was deposited on the surface of a silicon plate and the latter was heated in air for 5 min at 700–1000°C. This resulted in the appearance of dispersed platinum on the silicon, which served as a carrier.

The use of electrolysis and of the thermal decomposition of chemical compounds for the preparation of disposed metals made it possible to obtain by a relatively simple technology catalysts with a comparatively high activity. Direct deposition of platinum and palladium blacks and of dispersed silver on a nichrome carrier or on the surface of the specimen being oxidised, for example, silicon, makes it possible to reduce the consumption of platinum, palladium, and silver under these conditions.

The degree of dispersion of the catalysts was determined by X-ray diffraction[98]. The average size of the crystals was 15, 230, and 2650 Å for palladium, platinum, and silver respectively, which corresponds approximately to the following specific surfaces ($m^2\ g^{-1}$): 370 for Pd, 12 for Pt, and 2.2 for Ag.[26,89,90].

2. THE ACCELERATING CATALYTIC EFFECT OF CATALYSTS ON THE OXIDATION OF TITANIUM, SILICON, GERMANIUM, AND GALLIUM ARSENIDE

(a) Catalysis of the Oxidation of Titanium

There is virtually no information in the literature about the kinetics of the growth of interference oxide layers on titanium in the presence of catalysts. We investigated

the catalytic oxidation of titanium by air in the presence of dispersed platinum, palladium, and silver in the temperature range 400–550°C.[88–92] The interference colours of the films were used as the indicator. Specimens of the OT4-0 titanium alloy (Ti ⩾ 96.5%), subjected to mechanical polishing to a roughness class of 10–12, were used in the experiments. A study was made of the kinetics of the film growth within the limits of the formation of the yellow–brown–violet–dark blue–blue first-order spectrum with the catalyst arranged parallel to the surface of the specimen being oxidised and in contact with it[99]. On formation of interference rutile films (TiO_2), the local catalytic action of platinum, palladium, and silver was observed for the first time. It was found that in the presence of these metals the rate of growth of the oxide layer in the region of direct contact between the catalyst and the specimen is much higher compared with the rest of the surface. Thus at 400°C the formation of a blue film in the absence of a catalyst takes place over a period of 130 h and 45 min, while in the presence of platinum the reaction takes 4 min and 12 s, i.e. the oxidation of titanium is accelerated by a factor of 1868. The degree of acceleration of the oxidation process depends on the nature of the catalyst employed, the temperature of the reaction zone, and the thickness of the film formed (Tables 9 and 10). Table 10 presents a quantitative estimate of the parameter of the local-catalytic acceleration (K) of the titanium oxidation reactions in the presence of the platinum and silver catalysts, K being defined as the ratio of the times required for the formation of the TiO_2 interference film with a standard colour in the absence and in the presence of a catalyst.

Table 9. Time required for the formation of interference rutile films in the catalyst–specimen contact zone[89,90].

Colour of film	Catalyst	Time, min			
		400° C	450° C	500° C	550° C
Brown	None	780	47	7.17	4.2
	Dispersed Ag	5.00	2.5	1.75	1.20
	Pt black	2.25	1.5	1.00	0.83
Violet	None	2970	270	26.42	10.75
	Dispersed Ag	6.5	3.00	2.17	1.33
	Pt black	3.15	1.85	1.30	1.00
Dark blue	None	5520	1140	85	19.66
	Dispersed Ag	8.1	4.6	3.17	1.83
	Pt Black	3.75	2.1	1.42	1.20
Blue	None	7845	2520	270	66
	Dispersed Ag	10.2	6.75	4.08	2.55
	Pt Black	4.2	2.4	1.6	1.35

The data presented in Tables 9 and 10 show that, with increase of the thickness of the TiO_2 oxide layer, the efficiency of the catalyst increases. Thus at 400°C platinum black accelerates the formation of the brown rutile film by a factor of 346, the violet film by a factor of 943, the dark blue film by a factor of 1470, and the blue film by a factor of 1868. With increase of temperature, the activity of the catalyst falls. For example, dispersed silver accelerates the formation of the violet rutile film by a factor of 457 at 400°C, 90 at 450°C, 12 at 500°C, and 8 at 550°C.

A difference between the catalytic activities of platinum, palladium, and silver was observed by the method of interference indication. The initial stages in the oxidation of the test alloys in the presence of platinum black take place at a higher rate than in the presence of dispersed silver. Thus the formation of a blue film on specimens of type OT4-0 at 400°C in the presence of platinum and silver catalysts takes place after 220 and 610 s respectively.

Table 10. The local catalytic acceleration (the values of K) for the oxidation of the OT4-0 titanium alloy in the presence of platinum and silver[89].

Colour of film	Pt				Ag			
	400° C	450° C	500° C	550° C	400° C	450° C	500° C	550° C
Brown	346.6	31.3	7.1	5.0	158	18.8	4.0	3,5
Violet	942.8	145.9	20.3	10.7	456.9	90.0	12.1	8.0
Dark blue	1472	542.8	59.8	16.3	681.5	247.9	26.8	10.7
Blue	1867.8	1050	168.7	48.8	771.2	373.0	66.0	25.8

(b) Catalysis of the Oxidation of Silicon

Polished plates of type KEF, oriented in the (111) plane, which catalysed oxidation by atmospheric oxygen in the range 450–1350°C, were used in the experiments on the catalytic oxidation of silicon[117,118,129]. The platinum, palladium, and silver catalysts, deposited on carriers in the form of a needle, were mounted with the aid of a special device over the silicon plate undergoing oxidation at right angles to its surface[117,118].

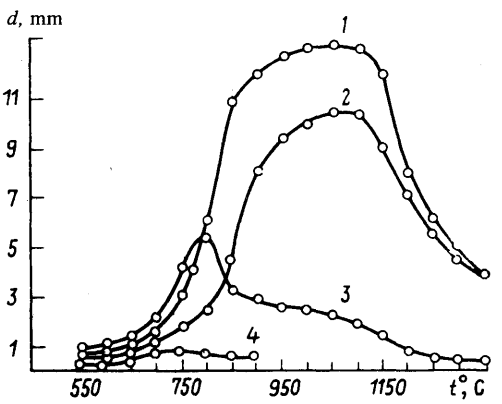


Figure 9. Dependence of the diameter d of the interference zone in the oxidation of silicon on temperature for platinum black (curves *1* and *2*), palladium black (curve *3*), and dispersed silver (curve *4*); wire carrier: *1*) and *3*) platinum; *2*) nickel–chromium; *4*) silver; oxidation time 5 min.

The observation of a sharp increase in the rate of oxidation of silicon in the presence of platinum, palladium, and silver must be regarded as the principal result of these experiments[92,109,117,118]. For example, at 700°C the rate of growth of the blue SiO_2 film with a thickness of 1500 Å increases by a factor of 10^4 in the presence of the platinum

catalyst. Comparison of the silicon oxidation times in the presence and absence of platinum black showed[92] that K increases with decrease of temperature and with increase of the thickness of the oxide layer obtained.

The diameter of the interference zone in the catalytic oxidation of silicon depends on the type of the catalyst, temperature, and oxidation time. Thus in the course of 5 min the diameter of the interference zone reaches its maximum value at 1000–1100°C for platinum black, at 800°C for palladium black, and at approximately 750°C for dispersed silver (Fig. 9).[117,133] Platinum and silver are characterised by the greatest and smallest zone diameters respectively.

A marked weakening of the catalytic activity of the metals takes place at the temperature of the most effective sintering and recrystallisation, which is usually two-thirds of the melting point. Indeed, Fig. 9 shows that a sharp decrease in the diameter of the interference zone begins at 1100–1150°C for platinum and palladium black. The diameter of the interference zone also depends on the type of carrier employed. Thus the use of platinum as the carrier for platinum black results in a zone with a larger diameter than in the case of nichrome (Fig. 9).

Comparison of the times required for the formation of a silicon dioxide layer 15400 Å thick at 700°C in the presence of platinum and palladium blacks and dispersed silver shows that the activities of these catalysts increase in the sequence Ag < Pd < Pt.

The influence of geometrical factors, particularly of the length and thickness of the layer of catalytically active substance deposited on the carrier as well as its distance from the surface of the specimen, has been studied[119]. The experiments were performed with two arrangements of the catalyst (Fig. 10): (a) platinum (or palladium) black was at a distance s from the end of the needle; (b) platinum (or palladium) black covered the wire carrier over a length l from the point of its contact with the specimen.

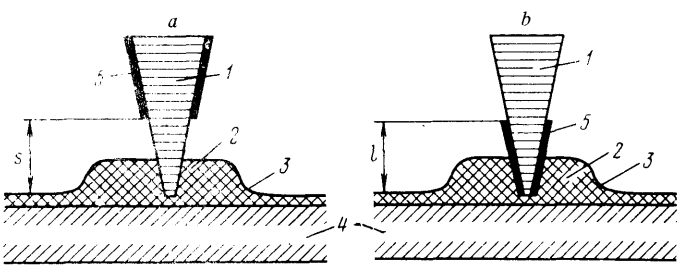


Figure 10. Schematic illustration (*a*) and (*b*) of the positioning of the catalyst relative to the silicon specimen: *1*) platinum or nichrome needle; *2*) SiO_2 film; *3*) interference colour rings; *4*) silicon plate; *5*) platinum or palladium black.

It was found that an increase of s reduces the catalytic effect. The catalytic effects of platinum black deposited on platinum and nichrome carriers differ significantly. The thickness of the SiO_2 film grown over a period of 5 min is independent of the extent l of the blackened section of the platinum wire.

Thus, with the aid of platinum, palladium, and silver catalysts, it is possible to achieve the local growth of oxide layers on silicon at temperatures of approximately 500–600°C at which the process virtually does not occur in the absence of the catalyst. The rate of the process depends significantly on temperature, the type of catalyst employed, and the distance of the active substance on the carrier from the silicon specimen.

The kinetics of the catalytic oxidation of silicon were determined by the mathematical treatment of the curves for the increase in the thickness in the SiO_2 film[129] obtained using platinum or silver foil, in contact with the surface of the specimen undergoing oxidation, as catalyst carriers. It was established that an increase of the film thickness with time is linear in the presence of platinum black and parabolic in the presence of palladium black and dispersed silver (Table 11). The activation energy for the oxidation process depends on the type of the catalyst. The oxidation of silicon in the presence of platinum black proceeds with a lower activation energy than in the presence of palladium black and dispersed silver; the activation energies at 500–700°C are 9.16, 9.75, and 12.76 kcal mole^{-1} respectively.

Table 11. Variation of the SiO_2 film thickness (y, Å) with time (τ, min) in the oxidation of silicon in air in the presence of catalysts[129].

Temperature, °C	Pt black	Dispersed silver	Pd black
500	$y = 1042\ \tau$	$y^2 = 33.16 \cdot 10^4\ \tau$	$y^2 = 80.66 \cdot 10^4\ \tau$
600	$y = 2329\ \tau + 3 \cdot 10^3$	$y^2 = 83.26 \cdot 10^4\ \tau$	$y^2 = 189.33 \cdot 10^4\ \tau$
700	$y = 3550\ \tau + 5.2 \cdot 10^3$	$y^2 = 121.93 \cdot 10^4\ \tau$	$y^2 = 444.66 \cdot 10^4\ \tau$

The equations for the rate constants for the catalytic oxidation of silicon, determined from the experimental data, are presented in Table 12, For the platinum catalyst, they are evidently different in the temperature ranges 500–700°C and 800–900°C.

Table 12. Dependence of the equations of the rate constants for the growth of the silicon oxide film on the type of catalyst employed and temperature[133].

Catalyst	500–700° C	800–900° C	Dimensions of rate constant
Pt black	$k = 4.08 \cdot 10^5 \exp(-4.62/T)$	$k = 1.86 \cdot 10^6 \exp(-5.01/T)$	A min^{-1}
Pd black	$k = 3.39 \cdot 10^9 \exp(-6.44/T)$	—	A^2 min^{-1}
Dispersed Ag	$k = 1.95 \cdot 10^8 \exp(-4.93/T)$	—	A^2 min^{-1}

The time (τ, s) corresponding to the appearance of SiO_2 films whose thickness corresponds to complete second-order (3500 Å) and eighth-order (15400 Å) colour spectra in the presence of platinum black varies with temperature in the following manner[129]:

For 3500 Å: $\tau \simeq 8.79 \times 10^{-2} \exp(5730/T)$, $E \simeq 11350$ cal mole^{-1};
For 15400 Å: $\tau \simeq 8.67 \times 10^{-4} \exp(11950/T)$, $E \simeq 27700$ cal mole^{-1}.

With increase of the oxide film thickness, the activation energy E for the oxidation of silicon increases.

Table 13 lists the times corresponding to the formation of SiO_2 films of different thickness in the isothermal oxidation of silicon in air in the presence (τ_2) and absence (τ_1) of $H_2[PtCl_6]$ at 700–1000°C and the increments in the rate of oxidation ($K = \tau_1/\tau_2$).[133] Evidently an increase of temperature lowers the efficiency of the catalyst.

Table 13.

Temperature, °C	SiO_2 film thickness, A	τ_1, min	τ_2, min	K
700	750	10 000	5	2000
800	1250	2 500	5	500
900	1500	700	5	140
1000	1750	300	5	60

(c) Catalysis of the Oxidation of Germanium

On direct contact with the specimen undergoing oxidation, platinum or palladium black leads to a local acceleration of the oxidation of germanium of type GES [32,90,91,109] at temperatures above 350°C (Table 14).

Table 14. Time required for the formation of the interference films in the catalyst–germanium specimen contact zone[90].

Colour of GeO_2 film (order of spectrum)	Catalyst	Time, min			
		350° C	400° C	450° C	500° C
Dark blue (I)	Pt black	5.0	3.25	1.0	0.75
" "	Pd black	10.1	5.4	1.5	1.1
Blue (I)	Pt black	6.0	4.0	1.25	1.0
" "	Pd black	15.3	7.1	1.8	1.25
Yellow (II)	Pt black	7.5	5.0	1.5	1.2
" "	Pd black	>30	8.7	2.2	1.4
Red(II)	Pt black	9.0	5.5	2.0	1.5
" "	Pd black	—	10.2	3.1	1.7
Green (II)	Pt black	10.0	6.25	2.5	1.8
" "	Pd black	—	13.5	4.25	2.1
Green (III)	Pt black	>30	7.5	3.0	2.1
" "	Pd black	—	17.1	5.1	2.8

It was found (Table 17) that, in the formation of interference oxide layers on germanium platinum is more active than palladium. The use of platinum and palladium catalysts makes it possible to oxidise germanium at an appreciable rate at approximately 400°C, i.e. 200° below the temperature in the absence of catalysts.

(d) Catalysis of the Oxidation of Gallium Arsenide

On heating in air, gallium arsenide begins to be oxidised at an appreciable rate above 600°C.[36,37] However, the use of the thermal oxidation method is significantly restricted by the fact that, on heating above 600°C, gallium arsenide crystals decompose appreciably to liquid gallium and gaseous arsenic in accordance with the equation

$$4GaAs(solid) = 4Ga(liq.) + As_4(gas).$$

A decrease of temperature and an increase of the rate of oxidation of GaAs are therefore of great practical interest.

In the presence of a platinum catalyst in contact with the specimen surface being oxidised the rate of oxidation of GaAs increases appreciably. Table 15 shows that the increase of the rate is greater the greater the thickness of the oxide layer.

Table 15. Dependence of the GaAs oxidation time in the absence (τ_1) and presence (τ_2) of platinum black and of the increment in the rate of oxidation $K = \tau_1/\tau_2$ on the thickness of the Ga_2O_3 oxide film[133].

Colour of β-Ga_2O_3 film (order of spectrum)	τ_1, min	τ_2, min	K
Brown (I)	1050	0.33	3150
Violet (I)	1350	0.41	3220
Dark blue (I)	1800	0.75	3600

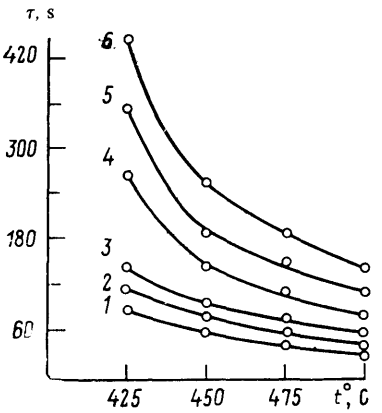


Figure 11. Temperature variation of the oxidation time τ of gallium arsenide in the presence of the platinum catalyst in contact with the specimen under-going oxidation before the appearance of brown (curve *1*), violet (curve *2*), dark blue (curve *3*), blue (curve *4*), yellow (curve *5*), and orange (curve *6*) oxide films.

The employment of platinum black reduces the GaAs oxidation temperature and makes it possible to obtain on the latter oxide films at a technologically acceptable rate at temperatures in the range 425–500°C (Fig. 11). The activation energy for the catalytic oxidation of GaAs varies in the range 9.4–21.1 kcal mole^{-1}.

3. THE INFLUENCE OF CATALYSTS ON THE OXIDATION OF TITANIUM, SILICON, AND GERMANIUM AT A DISTANCE

The catalytic oxidation of titanium, silicon, and germanium has been carried out[26,27,32,88–92,109,110,117–119] both with direct contact between them and dispersed metals and with the specimens undergoing oxidation placed at a certain distance from the catalyst. It was observed[27,89,90] that platinum and palladium coated with the corresponding blacks exert a catalytic influence on the rate of oxidation of titanium, silicon, and germanium placed at some distance from the catalyst (Tables 16–18). This effect begins to be observed at approximately 400°C. Table 17 shows that the growth of the SiO_2 film is observed in the course of approximately 4 min from the start of the oxidation; the subsequent reaction entails hardly any change in the thickness of the oxide film. An increase of the oxidation temperature (above 1000°C for platinum and above 800°C for palladium) lowers the catalytic influence of the dispersed metals (Fig. 12). The activity of the catalyst decreases with increasing distance between the dispersed metal and the specimen being oxidised. The catalytic activity of platinum black is higher than that of palladium black (Tables 16–18).

Table 16. Time required for the formation of rutile interference films with the catalyst acting at a distance (500°C).[89]

Distance from catalyst to specimen, mm	Catalyst	Time, min			
		brown film	violet film	dark blue film	blue film
0.1	Pt black	1.5	2.0	3.0	4.1
0.1	Pd black	1.5	2.3	3.7	4.8
0.5	Pt black	5.0	5.8	6.5	7.5
0.5	Pd black	5.0	6.9	8.0	10.0

Table 17. Dependence of the SiO_2 film thickness on the growth time at 650°C.[27]

Catalyst	Distance, mm	Film thickness, Å					
		1 min	2 min	3 min	4 min	5 min	6 min
Pt black	0.1	2000	2500	3900	5400	5400	5400
Pt black	0.4	1500	2000	3000	4260	4260	4260
Pt black	0.8	1000	1250	1500	2000	2000	2000
Pd black	0.1	1750	2000	2500	3500	3500	3500
Pd black	0.4	1250	1500	1750	2500	2500	2500

4. EXOELECTRON EMISSION FROM THE SURFACES OF DISPERSED PLATINUM, PALLADIUM, AND SILVER

The application of the method of exoelectron emission[120–123] makes it possible to obtain information about the energetic inhomogeneity, the density of defects, and the number of active centres on the surfaces of the catalysts investigated.

Exoelectron emission from the surfaces of compact platinum and platinum and palladium blacks was studied in a vacuum of approximately 10^{-5} mmHg on a specially designed apparatus[124] permitting the heating of the test catalyst to 400°C. An appreciable increase of the intensity of exoemission from the surfaces of the dispersed metals relative to the background level was observed on platinum black from 300°C, on palladium black from 350°, and on compact platinum from 370°C (Fig. 13). The most intense exoemission was observed for platinum black and the least intense for compact platinum. Evidently the energy of the liberation of the electron from the surface of platinum black is lower than from the surface of palladium black and compact platinum; in terms of increasing numbers of active centres, the catalysts can be arranged in the sequence compact platinum < Pd black < Pt black.

Table 18. Dependence of the time required for the formation of GeO_2 interference films and of the increment in the rate of oxidation of germanium (K) on the type of catalyst (450°C).[90,133]

Catalyst	Distance from catalyst to specimen, mm	Colour of GeO_2 film (order of spectrum)					
		dark blue (I)	blue (I)	yellow (II)	red (II)	green (II)	green (III)
		Time, min					
Pt black	0.1	1.0	1.5	2.0	2.5	3.0	4.0
Pt black	0.5	3.2	4.3	5.15	5.5	6.0	7.0
Pd black	0.1	3.0	4.5	5.0	6.0	7.0	9.0
Pd black	0.5	3.5	5.0	6.0	7.0	9.0	15
		K					
Pt black	0.1	1924	2198	2514	2841	3306	3620
Pt black	0.5	642	760	1005	1282	1651	2058
Pd black	0.1	602	731	977	1184	1416	1600
Pd black	0.5	550	658	838	889	1100	—

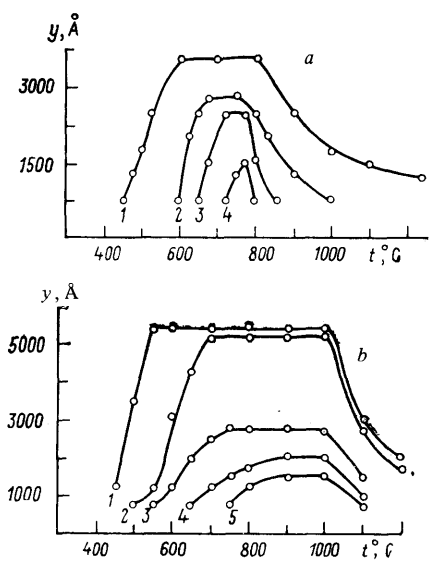


Figure 12. Temperature dependence of the SiO_2 film thickness in the oxidation of silicon in the course of 5 min in the presence of palladium (*a*) and platinum (*b*) catalysts: distance of the catalyst from the specimen surface (mm): *1*) 0.1; *2*) 0.4; *3*) 0.8; *4*) 1.0; *5*) 1.2.

5. GENERAL CHARACTERISTICS AND MECHANISMS OF THE REACTIONS INVOLVING THE CATALYTIC OXIDATION OF THE METALS AND SEMICONDUCTORS INVESTIGATED

Analysis of the experimental data for the catalytic acceleration of the oxidation of titanium, silicon, germanium, and GaAs by platinum, palladium, and silver[26,27,32,88-92,109,110,117-119,129] reveals the following features.

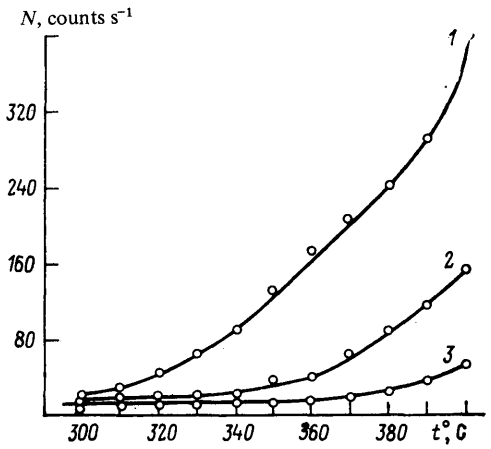


Figure 13. Temperature dependence of the intensity of exoelectron emission (N) from the surfaces of dispersed platinum (curve *1*) and palladium (curve *2*) and compact platinum (curve *3*).

Platinum, palladium, and silver catalysts accelerate the oxidation of the above metals and semiconductors above 350°C, the rate of reaction increasing by a factor of 100 to 1000. The catalyst accelerates the oxidation reactions both on contact and at a distance. The catalytic effect is more pronounced on direct contact between the catalysts and the specimens being oxidised. The catalysts accelerate the oxidation process in a zone directly adjoining them. The greatest catalytic activity among the dispersed metals employed is shown by platinum black and the smallest by dispersed silver.

In the presence of catalysts the Ti, Si, Ge, and GaAs oxidation temperature is reduced by hundreds of degrees and the rate of oxidation remains acceptable in practice. The efficiency of the catalysts increases with increasing thickness of the oxide layer formed (TiO_2, SiO_2, GeO_2 and Ga_2O_3).

Sintering of platinum and palladium blacks and of dispersed silver reduces the activity appreciably at temperatures amounting to two-thirds of the melting point of the catalyst. The difference between the laws governing the oxidation process in the presence of platinum, palladium, and silver catalysts (linear for platinum and parabolic for palladium and silver) is due to the unequal rates of their sintering, reducing the catalytic influence of the activated metals on the oxidation process.

The observed features can be accounted for in terms of modern ideas concerning the oxidation of metals and semiconductors[1,9,11,12,14,38-43,46,49-54,58,59,64,65,125] and heterogeneous catalysts[16,18,111-116,126-128].

The TiO_2, SiO_2, GeO_2, and Ga_2O_3 oxide films formed in the interaction of titanium, silicon, germanium, and gallium arsenide with oxygen cause a separation of the initial reactants in space. The subsequent reaction is limited by the migration of titanium, silicon, germanium, gallium, and oxygen ions through the growing oxide film. The diffusion process occurs in consequence of the generation of concentration gradients and of an electric field in the growing oxide layer[49-54]. The overall charge transfer current density j_i is then defined by the expression[14]

$$j_i = -c_i v_i (\Delta\mu_i + z_i e E) \ ,$$

where c_i is the concentration of species, v_i the mobility of the charges, $\Delta\mu_i$ the change in the chemical potential, z_i the valence of ions of type i, e the electronic charge, and E the electric potential gradient.

The large surface of the catalysts is capable of retaining considerable amounts of chemically adsorbed oxygen, the redistribution of which increases the oxygen concentration gradient in the oxide films and the electric field strength with increase of film thickness on metals and semiconductors. This increases the charge transfer current density and the rates of chemical interaction. In addition, the increase of the electric field strength lowers the activation energy for the oxidation process (for example, from 30-43 kcal mole^{-1} [9,11,12,14] to 9-13 kcal mole^{-1} [109,110,129,131] for silicon). As a result, the significant increase of the ionic diffusion flux density and the decrease of activation energy lead to an increase of the rate of oxidation in the presence of catalysts by factors of hundreds and thousands.

According to the existing electronic theories of heterogeneous catalysis[111,114,128], the gas, for example, oxygen, is activated by its chemisorption on the active centres of the catalyst surface and the activation is accompanied by the transfer of electrons from the catalyst to the adsorbed atoms. The amount of adsorbed oxygen is greater the greater the number of active centres from which electrons pass to oxygen comparatively readily. The results obtained by the method of exoelectron emission suggest that the number of these active centres is greater on platinum black than on palladium black. This apparently explains the higher catalytic activity of platinum black despite its smaller degree of dispersion.

The action of the catalysts at a distance can be accounted for in the following way. Evidently the activated species are dissolved from the catalyst surface into the surrounding gas phase[114,126-128]. With increase of temperature, this is accompanied by a displacement of the dynamic equilibrium towards desorption. The desorbed species retain their activity for some time at a short distance from the catalyst surface, after which they recombine[126,127]. Contact of the catalyst with the specimen undergoing oxidation facilitates the transfer of active oxygen species from the catalyst to the oxide film. This is why the catalytic activity of the activated metals is greater on contact than at a distance.

V. SOME PRACTICAL APPLICATIONS

The results presented in the present review permit practical recommendations for the use of the titanium, silicon, germanium, and gallium arsenide oxidation reaction.

Determination of the kinetic parameters of reactions. The kinetic parameters of heterogeneous reactions involving the oxidation of metals and semiconductors, for example, the activation energy, are determined by the mathematical treatment of data obtained as a result of the visual observation of the changes in the interference colours of oxide films in the course of the interaction. It is then possible to establish the dependence of the kinetic parameters of the reactions on temperature, the thickness of the interference film, the nature of the material being oxidised, and other factors.

It is possible to use TiO_2, SiO_2, GeO_2, and Ga_2O_3 interference films as decorative and protective coatings on the surfaces of metals, alloys, and semiconductors.

The accelerated formation of oxide films in the course of the oxidation reaction is achieved by employing platinum, palladium, and silver catalysts which are either in contact with the surface of the specimens being oxidised or are at some distance from them. The employment of catalysts permits the formation of films with the required thickness over a short time interval and at a lower temperature than in the thermal oxidation in the absence of catalysts.

The comparative activities of catalysts are determined by comparing the times required for the formation of oxide films of identical thickness in the presence (τ_1) and absence (τ_2) of the catalyst. The increase of the rate of oxidation $K = \tau_2/\tau_1$ can serve as a measure of the activity of the catalyst. Furthermore, the activity of the catalyst can be estimated approximately from the diameter of the interference zone (in this case it is necessary to employ a catalyst carrier in the form of a needle). In addition, the activity of the catalyst can be inferred from the intensity of the exoelectron emission, since the intensity increases with increasing number of active centres on the catalyst surface.

The marking of articles. The use of catalysts (acting on contact or at a distance) makes it possible to mark titanium, silicon, germanium, and gallium arsenide with appropriate symbols[132]. Such marking does not affect the surface oxide layer on the article and is distinguished by an improved thermal and corrosion resistance in corrosive media. Furthermore, in forming the symbol, the surface of the marked article is not strongly acted upon. All these factors lead to good prospects for the practical employment of heterogeneous catalysis in the oxidation of metals, alloys and semiconductors.

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Reactions in a Protein-Polymeric Carrier System Used for the Immobilisation of Enzymes

M.I.Shtil'man

The review is devoted to methods for the formation of a covalent bond between a polymeric carrier and enzymes whereby the latter are immobilised.
The bibliography includes 474 references.

CONTENTS

I.	Introduction	1109
II.	Acylation reactions	1109
III.	The azo-coupling reaction	1112
IV.	The formation of azomethine derivatives	1113
V.	The use of polyimidocarbonates	1113
VI.	The use of polymeric carriers containing isocyanato- and isothiocyanato-groups	1114
VII.	The use of polymers with an active halogen atom	1114
VIII.	Other methods	1115

I. INTRODUCTION

Enzymes immobilised in various ways in order to make them water insoluble have been attracting increasing attention recently. The preparations thus obtained (immobilised or stabilised enzymes) are used in chemical engineering, medicine, and analytical chemistry.

Numerous reviews and a series of monographs devoted to the immobilisation techniques and the characteristics of the employment of such artificial catalysts have been published in recent years in both foreign and Soviet literature[1-14]. A special review deals with kinetic-thermodynamic aspects of catalysis by immobilised enzymes[15]. Problems of the immobilisation of enzymes have been considered in a fundamental publication by a team of workers from Moscow University[16]. There is no doubt that the greatest number of studies on immobilisation methods have been devoted to methods involving the formation of a covalent bond between the enzyme and the carrier, particularly a polymeric carrier. The number of publications in this field is continuously increasing. Nevertheless, we believe that the extensive information about this important field of reactions between proteins and synthetic or artificial polymers has been inadequately dealti with in the review literature.

The immobilisation of enzymes by their attachment via a covalent bond to a polymeric carrier is based on the interaction of the reactive groups in the macromolecules of the polymeric carrier and the protein. In principle, the following functional groups forming part of protein aminoacids can react[4,16,17]: carboxy-groups (terminal groups and the groups in glutamic and aspartic acids), amino-groups (terminal groups and the groups of lysine and hydroxylysine), phenolic groups (in tyrosine), imidazole groups (in histidine), indole groups (into tryptophan), sulphydryl groups (in cysteine), disulphide groups (in cystine), hydroxy-groups (in serine, hydroxyproline, hydroxylysine, and hydroxyglutamic acid), guanidino-groups (in arginine), methylthio-groups (in methionine), phenyl groups (in tyrosine and phenylalanine), amido-groups (in asparagine and glutamine), and in certain cases peptide groups. In many cases it is difficult to determine with which protein group the carrier group reacts. For example, the acylating groups of the carrier can react both with amino- and with hydroxy- and mercapto-groups of the enzyme. The steric disposition of the reacting molecules plays an important role in such reactions.

A number of conditions must be observed in the immobilisation process. In particular, the reaction must proceed under conditions which rule out the denaturation of the protein. Furthermore, the functional groups of the carrier must not react with the groups of the protein responsible for enzyme activity[5].

Unfortunately the mechanisms of the reactions used to bind enzymes to polymeric carriers are obscure in many instances. This hinders significantly the classification of the known processes. However, among these one encounters both substitution and addition reactions involving aliphatic and aromatic carbon atoms as well as reactions at heteroatoms which proceed mainly via heterolytic mechanisms. Radical processes are used much more rarely.

II. ACYLATION REACTIONS

Amino-, hydroxy-, mercapto-, and guanidino-groups of enzymes can be involved in acylation reactions under the influence of the carrier. Although amino-groups are the most reactive, the mode of reaction depends significantly on many factors, particularly steric factors, the pH of the medium, etc.[4]

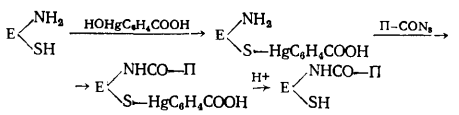
1. Acylation by Polymeric Azides

One of the first studies on the covalent binding of proteins to synthetic or artificial polymers was that of Micheel and Evers in 1949,[18] who used for this purpose carboxymethylcellulose activated by conversion into the azide[18]. In essence, this method is a modification of the familiar azide method for the synthesis of peptides proposed by Curtius in 1902.[19]

In this case the chemical reactions can be represented schematically as follows†:

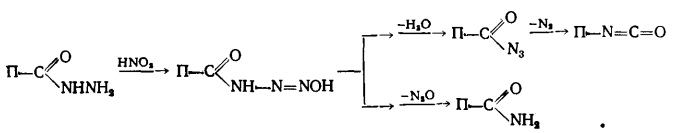
$$\text{П—OCH}_2\text{COOH} \rightarrow \text{П—OCH}_2\text{COOC}_2\text{H}_5 \rightarrow \text{П—OCH}_2\text{CONHNH}_2 \rightarrow$$
$$\rightarrow \text{П—OCH}_2\text{CON}_3 \xrightarrow{\text{H}_2\text{N—E}} \text{П—OCH}_2\text{CONH—E}$$

The stage involving the interaction of the azide with the functional groups of the protein takes place at 0–5 °C in the course of 1–2 h in a weakly alkaline medium. Under these conditions, azides react preferentially with amino-groups; however, they can also react with hydroxy- and mercapto-groups. Since the latter are frequently involved in the active centre of the enzyme, an attempt is made to avoid the formation of thioesters in such cases. For this purpose, mercapto-groups, for example, are temporarily protected by the introduction of an organomercury residue by reaction with *p*-hydroxymercuribenzoic acid. After the reaction with the carrier has been carried out, the protecting group can be removed in a weakly acid medium (10^{-6} M HCl):[4,20,21]



The azide method has been used fairly widely[20-32,34-69]; it has been examined more or less in detail in a number of reviews[1-8,16,69].

In the general case the immobilisation process is significantly complicated in view of the possible occurrence of a number of side reactions involving the azide group and its conversion products. In particular, when HNO_2 and hydrazides react, inactive amide and active isocyanato-groups can be formed together with azido-groups:



The isocyanato-groups can react in their turn with various groups of the protein (preferentially amino-groups), but after hydrolysis to amino-groups they can also give rise to urea groups in the carrier itself. All these factors require a rigorous observation of optimum reaction conditions (specified temperature, pH, etc.) (see Berezin et al.[16], p.159). The low stability of the azido-groups, which precludes the retention of activity by the carriers for a long time, also creates certain disadvantages. In recent years the azide method has been used fairly rarely.

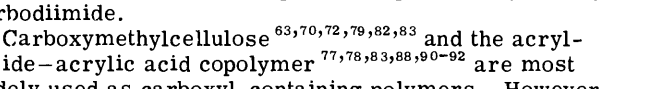
Carboxymethyl derivatives of polysaccharides, for example, cellulose and dextran, are usually employed as the carboxyl-containing polymers[33,50,60,63,69,165]. Using the azide method, it is possible to employ also polymers without carboxy-groups as carriers. Thus hydrazido-groups have been introduced[42] by treating a cross-linked polyacrylamide with hydrazine:

$$\text{П—CONH}_2 \xrightarrow{\text{H}_2\text{NNH}_2} \text{П—CONHNH}_2 .$$

A number of enzymes were immobilised on the resulting polyhydrazide (under the commercial name "Enzacryl AH") after its conversion into the azide[42,53-59]. The use of polyacrylic acid azide, which is soluble in borate buffer, for the binding of enzymes has also been described[44]. Among other carriers employed, one may mention the hydrazide derivative of agarose[66], the azide of polyglutamic acid[67], the copolymer of maleic acid azide with acrylamide and methylenebisacrylamide[68], and a polymeric azide obtained from the graft copolymer of cellulose and methyl acrylate[80].

2. Acylation in the Presence of Carbodiimides

The carbodiimide method, which has come to be fairly widely used, was also borrowed from peptide synthesis. Low-molecular-weight carbodiimides can be used as cross-linking agents independently without a polymeric carried; at the same time, numerous studies have been devoted to the activation of the carboxy-groups of the polymeric carrier by carbodiimides with subsequent attachment of the protein molecule[70-79,81-96]:



Water-soluble carbodiimides[78,87-90], for example, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride[88,95], 1-cyclohexyl-3-(*p*-diethylaminocyclohexyl)carbodiimide hydrochloride, and methyl toluene-*p*-sulphonate–1-cyclohexyl-3-(4-ethyl-2-morpholino)carbodiimide[90] (see also Berezin et al.[16], p.170) are sometimes used in this reaction instead of the most frequently employed dicyclohexylcarbodiimide.

Carboxymethylcellulose[63,70,72,79,82,83] and the acrylamide–acrylic acid copolymer[77,78,83,88,90-92] are most widely used as carboxyl-containing polymers. However, other polymers, for example, carboxy-methyl-Sephadex[82,83], Sepharose derivatives[87], polyamides[62], and the 2-hydroxyethyl acrylate–methacrylic acid copolymer[86] can also be used. α-Amylase has been attached to a carboxyl-containing carrier with the aid of carbodiimides[96]. A polypropylene fabric to which polyacrylic acid had been grafted and partially hydrolysed poly(ethylene terephthalate film) were used as carriers.

Other carriers were unsubstituted cellulose[4], copolymers of *N*-vinylpyrrolidinone and unsaturated acids[93], CH-Sepharose 4B, and AH-Sepharose 4B, containing the $-\text{OCONH(CH}_2)_6\text{COOH}$ and $-\text{OCONH(CH}_2)_6\text{NH}_2$ groups (Berezin et al.[16], p.172).

Valentova[89] used particles of hydroxyalkyl methacrylate gels (under the commercial name "Spheron") for the immobilisation of pepsin by this procedure. The gel particles were activated with bromide and then hexamethylenediamine or aminocaproic acid were grafted to it, which results in polymers containing carboxy- and amino-groups. The immobilisation was carried out in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide. Not only the carboxy-groups of the carriers but also, in principle, those of the enzyme can be activated by carbodiimide:

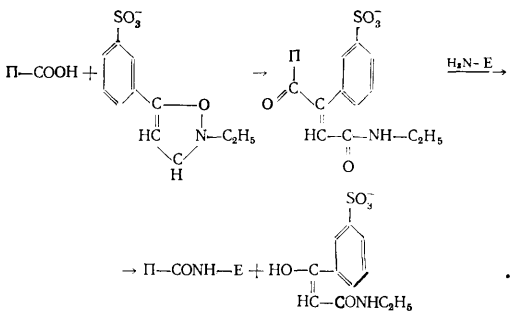
$$\text{E—COOH} + \text{H}_2\text{N—П} \xrightarrow{\text{R—N=C=N—R}} \text{E—CONH—П} + \text{R—NH—CO—NH—R} .$$

In this case the activated enzyme adds to the amino-polymer, for example, aminoethylcellulose[6]. Carboxyl-containing enzymes have been bound with the aid of dicyclohexylcarbodiimide to the product of the interaction of the ethylene–maleic anhydride copolymer with hexamethylenediamine[94].

† Here and henceforth π is the residue of the polymer chain of the carrier and E is the residue of the protein chain of the enzyme.

3. Acylation in the Presence of Woodward's Reagent

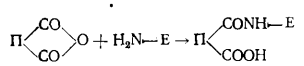
In 1961 Woodward et al.[97] described the use in peptide synthesis of activated esters obtained on the basis of *N*-ethyl-5-phenylisoxazolium 3′-sulphonate. Later this reaction was used[98,99] to obtained insoluble preparations with enzymatic activity; this method was also used in a number of other studies[41,100,101]:



Carboxy-containing polymers [carboxymethylcellulose[98] and the copolymer of L-alanine and L-glutamic acid (berezin et al.[16], p. 173)] have also been activated by Woodward's reagent. The advantage of this process is that it proceeds under fairly mild conditions[4]. Furthermore, in this case it is easy to regulate the number of active groups introduced into the carrier[5]. This method can supplement the carbodiimide method just discussed, since in the former the reaction proceeds in an alkaline medium and in the latter in an acid medium[4].

4. Acylation by Polymeric Anhydrides

The ability of polymeric anhydrides to interact in the cold with the protein molecules of enzymes (primarily with formation of amide groups) was first used probably in 1964[102,103] Subsequently this method gained wide currency[21,45,100,102-104,106-145]:



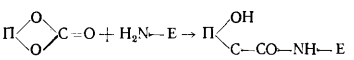
Mainly copolymers of maleic anhydride (see, for example, Refs. 46, 102, 103, 132, 134, and 139) were used. However, studies have been made on the use of copolymers of methacrylic acid anhydride[125,130] and also the anhydrides of itaconic and citraconic acids[133] and the homopolymer of the anhydride of methacrylic acid[208]. Ethylene[102,103,139], the divinyl ether of butanediol[45,131], ethyl vinyl ether and divinyl ether[133,134], methyl vinyl ether[136,144], and alkylene diacrylates[138] have also been used as comonomers with maleic anhydride.

Krömer and coworkers obtained and used for the immobilisation of enzymes a copolymer containing 32 mole % of methacrylic acid anhydride, 67 mole % of acrylamide, and 0.5–1.0 mole % of methylenebisacrylamide[125,130,143]. A homopolymer of maleic anhydride[142] and a number of other anhydride-containing polymers[145] have also been employed for immobilisation. In particular the anhydride groups intended for reaction with the protein molecule were obtained by heating to 180°C a copolymer of maleic acid, acrylamide, and methylenebisacrylamide[68].

The immobilisation on amino-carriers of the soluble products of the interaction of enzymes with a copolymer of ethylene and maleic anhydride has been described[137,140]. The influence of the number of anhydride groups in the carrier molecules on the activity of the enzyme has been investigated[141]. The copolymers of the anhydrides of unsaturated carboxylic acids can be used both in the form of beads and as films or coatings[132,136].

5. Acylation with Cyclic Carbonates of Polymeric Alcohols

This method was proposed by Kennedy and coworkers[146-154] and consists in the interaction of enzymes with polymers (mainly polysaccharides) containing *trans*-3,4-cyclic carbonate groups, which are introduced into the polymer by the reaction of the polymeric alcohol with ethyl chloroformate. The reaction with the protein proceeds via the following mechanism[154] at ~4°C in a citrate buffer solution at pH 5.4:

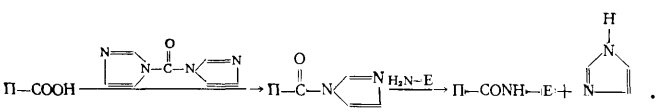


Later studies were carried out in which other polymeric alcohols[155], particularly polyallyl alcohol[153], were used for reactions of this kind.

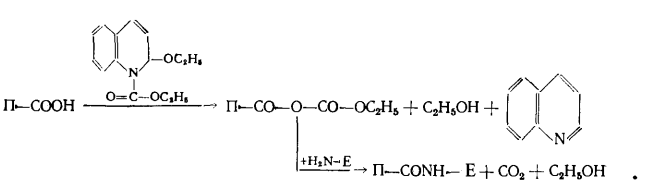
6. Other Acylation Methods

A number of other methods for immobilisation using acylation reactions, mainly reactions involving the formation of amide groups from the amino-groups of the protein molecule, have been developed in recent years.

Thus the copolymer of styrene and 4-vinylbenzoic acid has been used as a carrier[156-158], the reaction with the enzymes being carried out in the presence of carbonyldiimidazole in dimethylformamide:



The same workers suggested that the reaction of the carrier (the copolymer of 4-methacryloyloxybenzoic acid and divinylbenzene) with the amino-groups of enzymes be carried out in the presence of *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline introduced into the reaction as an activator[159,160]. The reaction evidently proceeds via a stage involving the formation of a mixed anhydride:

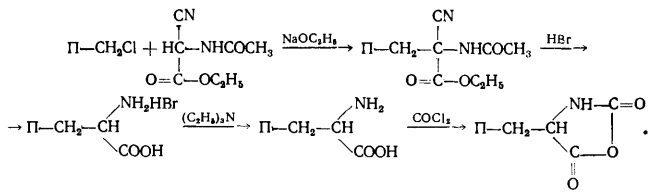


It has also been used by Sundaram[161], who used carboxymethyl-cellulose and carboxymethyldextran (Sephadex) as carriers.

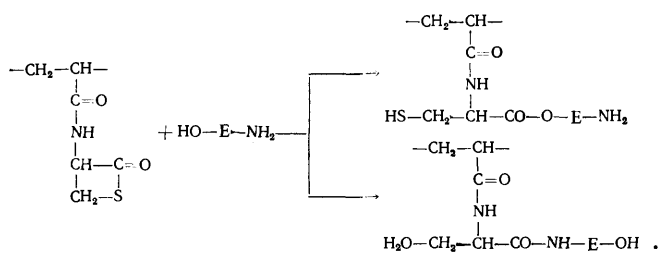
Polymeric acylating carriers containing acyl chloride groups have been described[162,164-166].

A polymeric cyclic *N*-carboxyanhydride, containing the 2,5-dioxa-4-oxaquinazolinedione group, has been used to bind a number of enzymes at 0°C in the course of 20 to 72 h.[167] This polymer was obtained from a chloromethylated polystyrene copolymer via the following

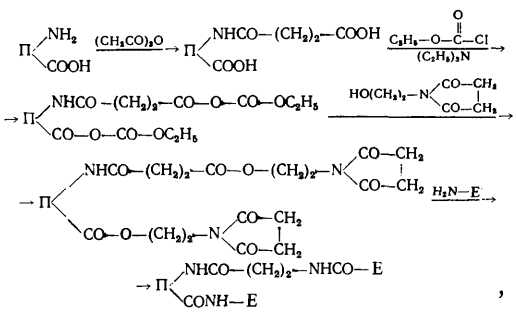
mechanism:



Derivatives of polyacrylamide or its copolymers containing thiolactone groups, manufactured under the commercial name "Enzacryl polythiolactone" can serve as acylating polymeric compounds [168,169]. This polymer can react with both amino- and hydroxy-groups of enzymes:



The use of polymeric carriers containing activated ester groups, for example, the copolymer of acrylamide and *p*-nitrophenyl acrylate [170], substituted cellulose [Cel–$OCH_2CH_2NHCO(CH_2)_2COOC_6H_4SO_2CH_3$] (see Berezin et al.[16], p. 167), polystyrene containing the $-CO(CH_2)_2-CO-O-C_6H_4NO_2$ group [171], and a partially hydrolysed polyamide in which the activated ester group with the alcoholic *N*-hydroxyethylsuccinimide residue was introduced by the procedure [172]

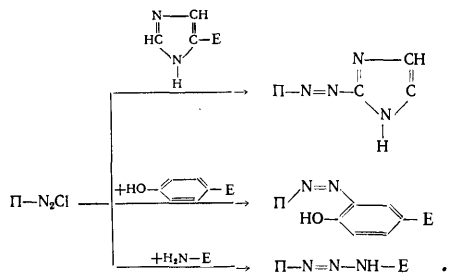


for the immobilisation of enzymes has been described.

III. THE AZO-COUPLING REACTION

The azo-coupling reaction has long attracted the attention of investigators in the field of the immobilisation of enzymes in view of its mild conditions and the ease with which the diazotisable aromatic amino-groups can be introduced into the carrier [173]. Later this reaction was employed in many investigations [26,34,38,42,70,102,104,109,112,163,169,174–202,204–207,209,211–243].

For example the following functional groups of the protein can be involved in the azo-coupling reaction:

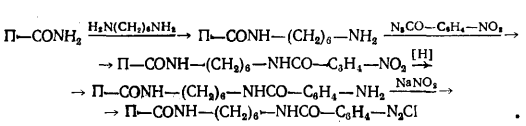


In addition, guanidino- and mercapto-groups can react with diazo-compounds. Under these conditions, two-diazo-groups can react with a single protein group [4].

The most frequently employed carriers are *p*-aminobenzylcellulose (see, for example, Refs. 26, 173, 174, 187, 188, and 235), *p*-aminostyrene (for example, Refs. 174–176, 199, 214, and 218), and copolypeptides based on *p*-aminophenylalanine (for example, Refs. 107, 177, 178, 184, 201, and 223). It has also been suggested that the product of the interaction of dialdehyde-starch and 4,4′-diaminodiphenylmethane be used as a diazotisable carrier [139,192]. On reacting with the aldehyde groups of dialdehyde-starch, the diamine forms a three-dimensional network. Among other carriers, we may mention the copolymer of glutaraldehyde and *m*-phenylenediamine [233], the reduced graft copolymers of *p*-nitrophenyl acrylate with poly(vinyl chloride), polypropylene, and polyethylene, and the styrene–propene copolymer [236], *p*-aminobenzamidohexyl Sepharose [237–240], polysaccharide anthranilates [221,226,227], aromatic amino-derivatives of polyacrylamide [169,209,210,219,220,225], the products of the interaction of a partially hydrolysed polyamide, aromatic diamines, diisonitriles, and aldehydes [234], aromatic amino-derivatives of wool, silk, chitin, and phenolic resins [241], and polyvinyl-(3-amino)benzylidene [242].

In order to obtain diazotisable carriers, the epoxy-resin based on di(hydroxyphenyl)propane and epichlorohydrin was treated with *p*-nitrophenylsulphonyl isocyanate with subsequent reduction of the nitro-group [243].

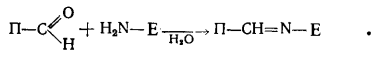
A multistage method has been proposed for the synthesis of diazo-derivatives of acrylamide [42]:



Diazotised aromatic diamines (benzidine-2,2′-sulphonic acid and *m*-phenylenediamine) have been used for the cross-linking of enzymes and polymeric carriers [107,197,205,211,224,228,232]. In order to increase the number of groups capable of undergoing the coupling reaction in the protein, the latter was treated with L-tyrosine *N*-carboxyanhydride [183]. The azo-coupling reaction has been used to bind not only enzymes but also other types of proteins, for example, antibodies, to the surface of the carrier [244].

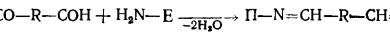
IV. THE FORMATION OF AZOMETHINE DERIVATIVES

Aldehydes react with the amino-groups of proteins under mild conditions with formation of Schiff bases:

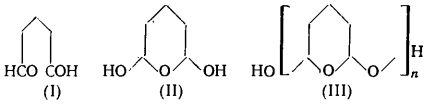


The characteristics of this reaction have been examined in detail in a review[105]. In recent years the reaction has served as the basis for one of the most vigorously developed procedures for the immobilisation of enzymes[21,88,94,171,245,247-253,255-298].

It is possible to isolate two trends in studies in this field—the use of polymers containing aldehyde groups (as shown in the above mechanism) and the use of low molecular weight aldehydes mainly glutaraldehyde) in order to bind enzymes to amino-carriers:



The glutaraldehyde used in the immobilisation reaction is in fact a fairly complex mixture of compounds. In particular, its aqueous solutions contain, apart from the aldehyde proper (I), also a low-molecular-weight cyclic acetal (II) and its oligomers (III). It has been stated (see Berezin[16], p. 208) that the mixture contains also derivatives of glutaraldehyde in which the α-position relative to the aldehyde group contains a double bond capable of involvement in an addition reaction with the amino-group[105]:



Among polymeric amino-carriers, aminoethylcellulose is most frequently used in combination with glutaraldehyde[21,245-247,250,257,277,287,290]. Among other amino-polymers, mention may be made of aminopolystyrene[21,171], partially hydrolysed polyamides[248,259-262,288,289], styrene–divinylbenzene copolymers modified by diamines[297], the maleic anhydride–ethylene copolymer treated with hexamethylenediamine[94], the products of the interaction of poly(methyl methacrylate) and 3-aminopropyltriethoxysilane[292], and polymers containing in the side chain lysine residues attached to the inner surface of a nylon tube activated with dimethyl sulphate[293]. Phenol-formaldehyde resins[241,265-267,275], gelatin[291], polyacrylamide[88,253], and certain other polymers[271,278] are also used for immobilisation in conjunction with glutaraldehyde.

A considerable number of studies have been devoted in recent years to the synthesis of polymers containing aldehyde groups in side chains and to their use as carriers for the immobilisation of enzymes. For these purposes, a number of acrolein derivatives were employed: the adduct of polyacrolein and sodium bisulphite[269,279,283], the acrolein–styrene copolymer[263], and the acrolein–acrylic acid copolymer[274]. The products of the partial oxidation of polysaccharides, accompanied by ring opening, particularly dialdehyde-cellulose[258,264,270,276], dialdehyde-Epidex[210,429], dialdehyde-dextran[280], ethoxycarbonyl-cellulose[249], the hydrolysis products of polymeric acetals[255,256,282,294], oxidised phenol-formaldehyde resins[256,241], polymeric derivatives of pyridoxal phosphate[239,240,295], polystyrene formylated by 1,1-dichloromethyl ether[171], copolymers of unsaturated aldehydes and vinylpyrrolidinone[93], and a polyacroleine reaction product[254] have also been made to react with enzymes.

The polymer of methacryloylvanillin {poly[4-formyl-2-methoxyphenyl methacrylate]} and its copolymers with allyl alcohols (p moles of allyl alcohol per mole of the aldehyde), known under the commercial names of Vanacryl and Covanacryl-p,[272,273,276,298] merit attention. Enzyme preparations immobilised on such carriers show a decrease of activity on storage in an aqueous medium, which is probably associated with the dissolution of part of the enzyme as a result of the hydrolysis of the ester group in the methacrylic acid residues[272,284].

Mention should also be made of a study[286] in which a method was proposed for the immobilisation of glucose oxidase on polyaminostyrene after preliminary oxidation (to give a 60% content of carbohydrate residues) of the enzyme with formation of aldehyde groups.

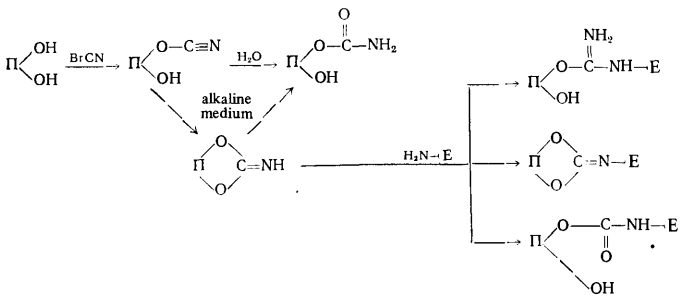
One should note that azomethine groups are insufficiently stable in acid media. In order to increase the stability of the polymer–protein system, it has been suggested that the azomethine groups be reduced with sodium tetrahydroborate[105,280,296]:



V. THE USE OF POLYIMIDOCARBONATES

The reaction of the amino-groups of proteins with polyimidocarbonates is widely used for the immobilisation of enzymes. These compounds are usually obtained by the reaction of polymeric alcohols with cyanogen halides (mainly with cyanogen bromide)[41,63,77,80,219,247,299-370]. This method has been proposed in two studies[299,300] and is attractive because of the high rate of reaction, the relatively high stability of the activated carrier, and its high reactivity in relation to the amino-groups of the enzyme.

The reaction proceeds via the following mechanism[5,335]:



The polyimidocarbonate, formed as the main product in the activation of a polyhydric alcohol, can give rise to an inactive unsubstituted carbamide in an alkaline medium. The carbamate can also be formed from the intermediate cyanate under the influence of water.

The reaction of imidocarbonates with the amino-groups of proteins can proceed via several pathways, which give rise to isoureas and N-substituted carbamates (urethanes). The formation of an interchain imidocarbonate, which can also interact with the amino-groups of the enzyme, is likewise very probable (see Berezin et al.[16], p. 176).

In the vast majority of studies polysaccharides are employed as the polyhydric alcohols: agarose (Sepharose)[77,88,238-240,290,294,296,307,308,316,317,321-323,330,339-343,347-353,354-367], dextran (Sephadex)[302,315-318,320-323,328,331,338,341,345,347,367-369], and (more rarely) starch[317] and cellulose[41,306,344,346]. Among other natural polymers, alginic acid has been used[370]; in this case the polymer–enzyme system is

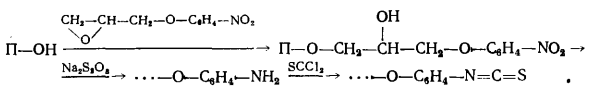
soluble at pH > 4, but is precipitated from solution at pH < 3. Synthetic polymers are used for these purposes much more rarely. In particular, the activation of the acrylamide–hydroxyethyl methacrylate copolymer with cyanogen bromide has been described [90]. Cyanogen chloride is much more rarely used for the activation of polymers in place of cyanogen bromide [371]. It has been stated that the imidocarbonate groups incorporated in the side chains of the polymer can be obtained by the interaction with polysaccharides with organic cyanates (see Berezin et al. [16], pp. 80 and 181).

Apart from enzymes, antibodies [372] and coenzymes [373] are also attached to carriers by the cyanogen bromide method.

VI. THE USE OF POLYMERIC CARRIERS CONTAINING ISOCYANATO- AND ISOTHIOCYANATO-GROUPS

Polymers containing these highly reactive groups have been used successfully for the immobilisation of enzymes despite their relatively high reactivity in hydrolysis [56,166,204,209,242,374–387]. Although, in principle, the isocyanato-groups can interact with many groups in the protein molecule (carboxy-groups—with formation of amides, hydroxy- and phenolic groups—with formation of urethanes, amide groups—with formation of acylureas, etc.), at the moderate temperatures used in the interaction with the protein, the amino-group is most reactive, giving rise to urea and thiourea groups on interaction with isocyanates and isothiocyanates.

Both artificial and synthetic polymeric carriers have been used for immobilisation. In particular, the following scheme has been proposed for the preparation of polysaccharides containing isothiocyanato-groups [246,378]:



Among the synthetic polymers used for immobilisation, mentioned may be made of the copolymers of methacrylic acid, *p*-aminostyrene, and 3,5-diisocyanatostyrene [380], the copolymers of methacrylic and acrylic acids and 3-isocyanatostyrene [379], and graft copolymers of polypropylene and *p*-nitrostyrene, whose amino-groups, generated by reduction, were treated with thiophosgene [204,385].

Synthetic polymers containing terminal isocyanato-groups in the main or side chains, such as polyureas based on hexamethylene diisocyanate and tolylene diisocyanate or hexamethylenediamine and triethylenediamine [166], polyethers with terminal isocyanato-groups [381], polyurethanes based on poly(propylene glycol) and tolylene diisocyanate [386,387], and products obtained by treating poly(allyl alcohol) with 4-isothiocyanatophenyl isocyanate [242] have also been used for immobilisation.

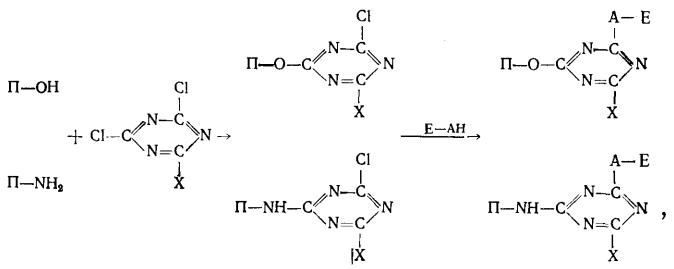
It has been suggested that the enzyme (trypsin) be treated initially with tolylene diisocyanate and that the resulting polyisocyanate be then cross-linked with poly(propylene glycol) [387].

VII. THE USE OF POLYMERS WITH AN ACTIVE HALOGEN ATOM

1. Polymers Containing Chlorotriazine Groups

In connection with the widespread use of carriers containing aldehyde and imidocarbonate groups, there has been some decrease in interest in recent years in polymers containing an active chlorine atom incorporated in a triazine group. However, studies in which polymers containing these groups are used for the immobilisation of enzymes are still being continued [63,163,195,206,388–412].

In this method the activated carrier is formed by the reaction of a polymer containing a group containing an active hydrogen atom (a hydroxy- or amino-group) with cyanuric chloride or a monosubstituted dichlorotriazine. The remaining unsubstituted chlorine atoms (atom) form hydrogen chloride by reaction with the protein molecule:



where X = Cl or R, A is the residue of a hydroxy-, amino-, guanidino-, phenolic, or SH group of the enzyme molecule.

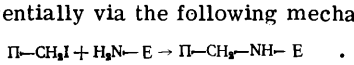
Among the polymers containing active atoms, polysaccharides (for example, Refs. 392, 398, and 410) or their aminoethyl derivatives (for example, Refs. 290, 308, and 399) have been most widely used. However, synthetic polymers, such as phenol-formaldehyde resins [409] and aminated polystyrene [171] have also been employed. Apart from cyanuric chloride, 2-amino-4,6-dichloro-*s*-triazine [63,290], 2-carboxymethylamino-4,6-dichloro-*s*-triazine [63], and Procion dyes [308] have been used to active these polymers.

Water-soluble derivatives of proteases have been obtained using a dextran modified with cyanuric chloride [93]. Arginase and urease have been attached with the aid of cyanuric chloride to different sides of a cellulose membrane [412]. The modification of enzymes by low-molecular-weight dichlorotriazine dyes followed by interaction with aminoethylcellulose has been described [407].

2. Polymers Containing An Active Halogen Atom Attached to Aliphatic and Aromatic Carbon Atoms

Publications about such carriers have appeared in the last 5–6 years. Thus it has been suggested that 4-iodo-n-butyl methacrylate polymers be employed; the exchange of a halogen in the reactions of monomeric and polymeric 4-chloro-n-butyl methacrylates with sodium iodide has been used to prepare such polymers [413–419].

The interaction of carriers of this kind with enzymes proceeds preferentially via the following mechanism:



Evidently other groups alkylated under these conditions can also react.

The copolymers of methacrylic acid and methacrylic acid 3-fluoro-4,6-dinitroanilide as well as the copolymers of these monomers with divinylbenzene [374-376,420-424] and the polymers and copolymers of fluorostyrenes and their derivatives [376,423] react similarly with enzymes.

Among other polymers containing an active halogen atom attached to aliphatic or aromatic carbon atoms used for the immobilisation of enzymes, we may mention bromo- and iodo-acetylcellulose [43,425,426], bromoacetamidohexyl-Sepharose [238-240,296], the products of the acylation of poly-(vinyl alcohol) with bromoacetyl bromide or bromoacetic anhydride [427], polyacrylamide derivatives containing iodoacetic acid residues [428], and 3-chloro-2-hydroxy-n-propyl-Epidex [429].

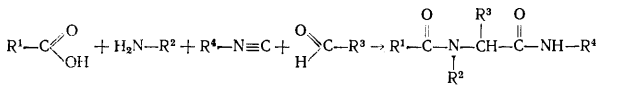
3. Polymers Containing Activated Halogen Atoms Forming Part of Inorganic Groups

Polymeric carriers containing activated halogen atoms in inorganic groups, mainly in inorganic acid residues, including acids derived from transition metals, are sometimes used. In particular, it has been suggested that synthetic polymers and polysaccharides be activated with thionyl chloride or sulphuryl chloride before interaction with enzymes [371,430,431]. A number of transition metal halides ($TiCl_4$, $SnCl_4$, VCl_3, $FeCl_2$, $FeCl_3$, and $ZrCl_4$), have also been used as activating agents. Both synthetic (polyamides) [432] and natural (cellulose [432-434] and chitin [435]) polymers have been treated with these compounds.

VIII. OTHER METHODS

1. The Use of Ugi's Method

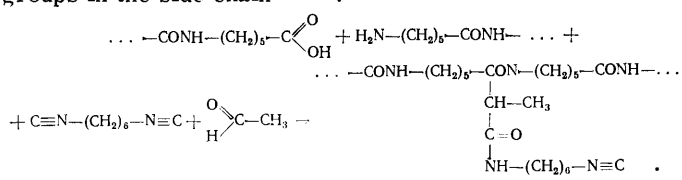
Ugi [436] showed that aldehydes (ketones), isonitriles, and carboxy- and amino-groups can interact:



This reaction has been used to bind a number of enzymes to polymeric carriers [437-443]. For example, Sepharose has been oxidised with formation of a polymer containing aldehyde groups. In the presence of 3-dimethylamino-propylisonitrile this polymer binds chymotrypsin at pH 6.5 in the course of 6 h. [438,439]

Carboxymethyl-Sephadex, aminoethylated polyacryl-amide [438], and a polyamine obtained by the interaction of diaminodiphenylmethane with Sepharose activated by cyanogen bromide [437] can be involved analogously in this reaction. The interaction of the last polymer with pepsin was carried out in the presence of phenylisonitrile and acetaldehyde.

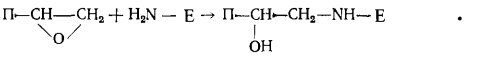
Another pathway leading to immobilisation involves the initial preparation of a carrier containing a sufficient number of carboxy- and amino-groups. A partly hydrol-ysed polycarproamide has been used for this purpose. The reaction of this polymer with hexamethylenediisonitrile and acetaldehyde yields a polyamide containing isonitrile groups in the side chain [442,443]:



Finally, the reaction of this carrier with trypsin in the presence of acetaldehyde results in the fixation of the enzyme.

2. The Reaction of Enzymes with Polymers Containing Epoxy-groups

Publications describing the immobilisation of enzymes and polymeric carriers containing epoxy-groups have begun to appear recently [444-449]:

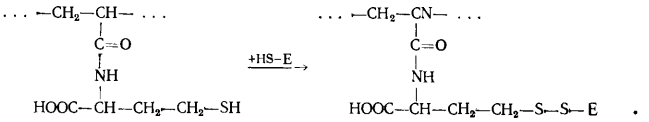


Thus the copolymers of epoxy-monomers (glycidyl meth-acrylate, glycidyl acrylate, and unsaturated glycidyl ethers) with other monomers, for example acrylonitrile and methacrylonitrile, have been used for this purpose [445,446]. The activity of the immobilised enzyme was higher when the carrier had been subjected to preliminary activation with an amine [444].

Urease was immobilised on a graft copolymer of carboxymethylcellulose and glycidyl methacrylate [447-449]. A method for the immobilisation of peroxidase, consisting in the copolymerisation with acrylamide of the enzyme subjected to a preliminary treatment with glycidyl meth-acrylate, is based on the ability of the amino-groups of proteins to react with epoxy-compounds [450].

3. The Thiol–Disulphide Exchange Reaction

The "Enzacryl polythiolactone" mentioned above can be attached to the mercapto-groups of enzymes when it is introduced into the reaction in the form of a mercapto-acid [169]:

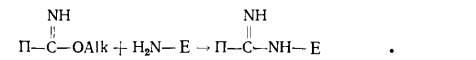


In order to increase the content of mercapto-groups in the initial enzyme, the latter can be subjected to a pre-liminary treatment with *N*-halogenoacetylcysteine thio-lactone [451] (see also Berezin et al. [16], p. 200).

Carlsson et al. [452] proposed another method for the immobilisation of enzymes (amylase and chymotrypsin) with the aid of the thiol–disulphide exchange reaction. The method includes two stages. In the first stage the NH_2 groups of the enzymes were modified with the aid of methyl 3-mercaptopropioimidate, which resulted in the introduction of a mercapto-group into the protein. In the second stage the enzyme with the mercapto-group was bound to disulphide derivatives of agarose obtained by treating the mercaptopropyl ether of the latter with 2,2′-dipyridyl disulphide.

4. Reactions with Polymeric Imidoesters

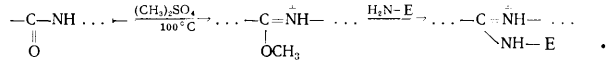
Polymers containing imidoester groups can interact with the amino-groups of proteins:



Thus Zaborsky introduced imidoester groups into a polyacrylonitrile powder by treating the latter with hydrogen chloride in methanol; this polymer was used as a carrier[453,454] and was also employed in a later study[456].

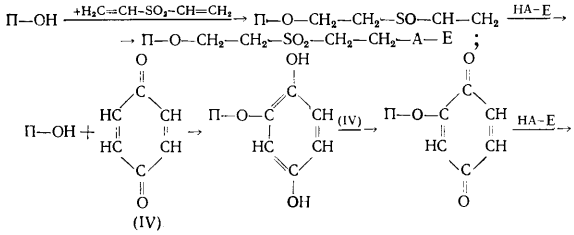
Imidoesters have been used also as cross-linking agents. In particular, a number of studies have been devoted to the interaction of enzymes and amino-polymers (aminoethylcellulose[455] and the products of the reaction of polyamides, activated by dimethyl sulphate, with lysine[293]) in the presence of diethyl adipimidate.

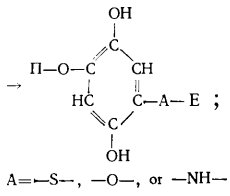
Yet another method for immobilisation (of glucose oxidase) using polymeric imidoesters has been proposed, namely on a polyamide treated with dimethyl sulphate[293]:



5. The Use of Carriers With an Activated Double Bond

Hydroxylated polymers can be activated by divinyl sulphone (Mosbach[460], p. 34) or quinone (Mosbach[460], p.35, and Tarasova et al.[461]). Such carriers can interact with the amino-, hydroxy-, or mercapto-groups of enzymes. The relevant processes can be represented schematically as follows:





(IV)

6. Radical Reactions

Radical procesees also play a definite role in the immobilisation of enzymes. This applies in the first place to the familiar processes involving the incorporation of an enzyme in a gel in the course of the polymerisation of unsaturated monomers (for example, acrylamide or its mixtures with methyl bisacrylamide, etc.), which is frequently accompanied by the formation of a covalent bond between the molecules of the enzyme and the gel-forming polymer as a result of a chain transfer reaction followed by grafting (see Berezin et al.[16], p.144). Cases of radical reactions in other systems are also known: for example, chymotrypsin is immobilised using the free radicals formed in aqueous solution as a result of ^{60}Co γ-irradiation[457]. Instances of the polymerisation of unsaturated derivatives of enzymes should also be classified as radical processes[458,459].

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This review shows that many processes have now been developed whereby enzymes can be linked by covalent bonds to polymeric carriers and that the possibility of introducing various functional groups into the latter is widely used. Naturally, in the course of the development of this field of enzyme immobilisation many methods have lost or are gradually losing their importance, giving way to more effective procedures (this can be seen from the analysis of the literature quoted). Polymeric carriers have been used in different forms—as grains, coatings, fibres, tubes, membranes, and gels.

Data, permitting the prediction to some extent of the efficiency of a particular carrier have now accumulated. Thus Porath formulated a series of properties, which the "ideal carrier" should possess: total insolubility in water; high chemical and biological stability; high mechanical stability; high reactivity with respect to the enzyme and ease of imparting such reactivity to the carrier; a form suitable for practical application; finally, highly hydrophilic properties of the carrier permitting its employment in aqueous media (see Berezin et al.[16], p.68). Some attention has been given in certain investigations to other properties of carriers, particularly their polarity (ionic and electrical effects[15,462]).

However, systematic studies have not so far been made of the influence of the nature of the carrier, particularly its chemical structure, geometrical structure, and molecular-weight distribution (for soluble forms) both on the characteristics of its binding to the protein and on the efficiency of the resulting biocatalysts. In the vast majority of studies quoted in this review very moderate attention has been devoted to these problems. According to the data quoted in many of the investigations, it is impossible to reach conclusions about the number of functional groups in the carrier responsible for the reaction with the protein, about the degree of their reaction in the course of binding to the enzyme, and about the influence of the conditions used in the preparation of the polymer–enzyme system on its catalytic activity.

As an example of a publication of this kind, one may quote the work of Baum[171], who compared the activities of immobilised amyloglucosidase and papain, obtained using polystyrenes containing different functional groups, and established that the carriers containing different groups (aldehyde, chlorotriazine, and activated ester groups) yield preparations with different activities. However, the author[171] does not state, for example, how many groups were present in each initial carrier nor is it stated what kind of carrier was used, particularly whether it was a linear homopolymer or a three-dimensional carrier obtained using a cross-linking agent. In our view, all these factors play a significant role in the preparation of effective biocatalysts. In this connection, one may refer to the known relation, with an extremum, between the content of functional groups in the initial carrier (ethylene–maleic anhydride copolymer) and the activity of the enzyme immobilised on this carrier[141].

Aspects of the influence of the chemical structure of the carrier on the properties of immobilised enzymes, which are already well known, such as the fact that the disposition of the active groups at the ends of side branches rather than in the main polymer chain is preferable[293], the negative influence of the enrichment of such branches

in aromatic groups (see Berezin et al.[16], p.188), the negative influence of the presence of hydrolytically labile groups at the carrier–enzyme binding sites[454,455], as well as the presence of groups promoting such hydrolysis (see Berezin et al.[16], p.166) have not been investigated in detail either.

All these findings show that detailed and systematic study of the influence of the properties of the carrier on those of the systems obtained can reveal considerable further possibilities for both an increase of the activity of the resulting preparations and for an increase of their efficiency. Studies in this field should probably be developed in the following directions: (1) investigation of the influence of the chemical structure and the physical properties of the carrier on the characteristics of the polymer–enzyme reaction; (2) investigation of the influence of the chemical structure and physical properties of the carrier on those of the immobilised enzyme obtained.

We believe that particular attention should be devoted to the following features of the chemical structure of the polymeric carrier: the content of functional groups and the degree of their utilisation in the reaction with the protein, the structure of the surrounding groups and sections of the polymer chain adjoining the carrier-enzyme binding site, and the structure and content of the groups responsible for the hydrophilic properties and polarity of the carrier.

In this connection mention should be made of the studies of Berezin and coworkers, who proposed a method using a carrier which is "complementary" to the surface of the enzyme globule and consists in the copolymerisation of a hydrophilic monomer (sodium methacrylate) and a cross-linking agent (methylene bismethacrylate) with an enzyme (chymotrypsin) modified by an analogue of the monomer (methacryloyl chloride). An increase of the thermal stability threshold of the enzyme by 40°C was achieved in this way relative to the native specimen[458,459].

It is quite possible that definite information about the characteristic features of the reaction between the carrier and the enzyme can be obtained from kinetic studies on the formation of the immobilised enzyme.

The study of the conformational changes in the enzyme occurring during its reaction with the carrier merits the closest attention. The importance of this factor was demonstrated by Martinek and coworkers, who showed that the activity of the enzyme (chymotrypsin) can change significantly as the extention of the nylon or viscose thread or the human hair to which it has been attached by covalent bonds is varied[285,288].

During the preparation of the review for the press, numerous publications in the field under consideration appeared in the literature, among which mention should be made of Refs. 463–474.

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The Synthesis and Properties of Polymeric Azaporphin Compounds

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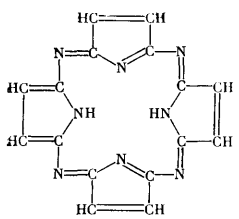
Data on the synthesis and principal properties of polymers with a conjugation system containing repeating azaporphin macrorings are surveyed and described systematically. An account is given of the change in properties on passing from metal-free polymers and their metal complexes, on the one hand, to the corresponding low-molecular-weight analogues, on the other. The bibliography includes 135 references.

CONTENTS

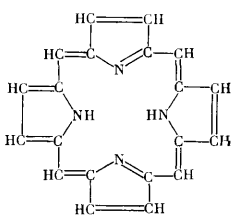
I. Introduction 1125
II. Principal methods of synthesis 1127
III. The study of structure 1129
IV. Certain physicochemical, electrical, and catalytic properties 1130

I. INTRODUCTION

The cyclic systems (I), consisting of four pyrrole rings linked together in the α-positions by nitrogen atoms, are called azaporphins† or porphyrazines, in contrast to porphins (II), which have a similar structure but the rings are linked by methylidyne groups:



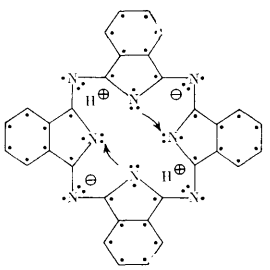
(I)



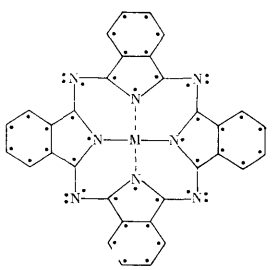
(II)

The pyrrole rings, which constitutes the basis of the azaporphin macroring, can be condensed with aromatic or heteroaromatic rings. Depending on the type of the latter, one can distinguish tetrabenzo-, tetranaphthalo-, tetrathiopheno-, and tetrafurano-azaporphins (tetrafuranoporphyrazines)[1,2]. Azaporphins whose pyrrole rings contain (usually in the 3- and 4-positions) various substituents—for example, octaphenyl-, dipropyl-, and octamethyl-porphyrazines, are known[2]. By analogy with porphins[3], such compounds could be usefully referred to also as azaporphyrins: octaphenyl-, dipropyl-, and octamethyl-azaporphyrins.

Despite the wide variety of porphyrazines, most investigations, among which those of Linstead, Vartanyan, and Berezin are the most important, were devoted to tetrabenzazaporphins, which are usually referred to as phthalocyanines. The structure and formulae of the metal-free phthalocyanine (III) and copper-phthalocyanine (IV) are given below‡:



(III)



(IV)

As can be seen from formula (III), as a result of internal dissociation the two protons of the imino-group of the azaporphin are subjected to the symmetrical electric field set up by the lone electron pairs of the nitrogen atoms[4,5]. These electrons are not localised at the opposite exocyclic nitrogen atoms but are uniformly distributed throughout the macroring, since their pairing would lead to the breakdown of conjugation. Thus 18 electrons move in the plane of the macroring, giving rise to a ring current of delocalised π electrons. This imparts aromatic§ properties and high stability to the azaporphin ring and determines the specific physical and physicochemical properties of compounds containing such rings.

The introduction of a metal in the "window" of the macroring (IV) entails the filling of the dsp^2-hybrid or other orbitals of the metal ion, which is accompanied by a change in the electron density at the peripheral nitrogen atoms and a consequent difference between the properties of the metal complexes and the metal-free analogues. The

†The abbreviation of tetra-azaporphins.

‡Henceforth in this review the following abbreviations will be used: PC = metal-free phthalocyanine, PC_M = phthalocyanine complexes of different metals (where M = Cu, Fe, Ni, etc.), PPC = metal-free polyphthalocyanine, PPC_M = polyphthalocyanine complexes of metals, PTCE = metal-free polytetracyanoethylene, $PTCE_M$ = polymeric metal complexes of tetracyanoethylene, and AA_M = metal acetylacetonates.

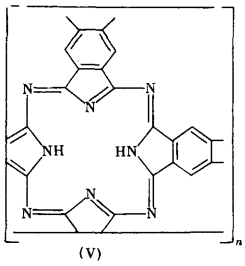
§The extreme aromatic nature of these compounds is indicated particularly by the finding that the magnetic anisotropy of phthalocyanine is approximately 15 times greater than that of benzene[6].

more covalent the >N–M–N< linkage, the greater the stability of the ring, and the greater the differences between the optical, magnetic, and electrical properties of the metal-free and metal-substituted porphyrazines[7-8].

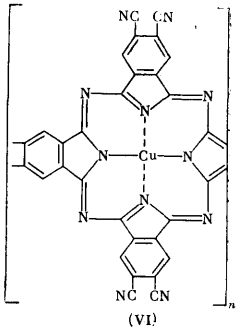
The unusual properties of phthalocyanines[9-12] stimulated the development of research on the synthesis of polymers containing azaporphin macrorings in their structure—polyazaporphins (PA) or polyporphyrazines. One might expect the possibility of the formation on the basis of these polymers of valuable materials combining the specific physicochemical and mechanical properties of high-molecular-weight compounds with the chemical and thermal stability, catalytic activity, and semiconductor properties characteristic of phthalocyanines.

The interest in systems of this kind is because the structure of PA resembles most closely (among the known synthetic polymers) that of natural compounds such as haemoglobin, chlorophyll, and the prosthetic groups of a number of enzymes (for example catalase). This fact is responsible for the exceptional importance of PA also as objects for the modelling of the biological activity of natural products.

All the PA known at the present time can be usefully divided into three groups differing in the nature of the functional groups joining the azaporphin rings in the macromolecule. The first group includes the PA in which the repeating units are joined via aromatic or heteroaromatic rings condensed to the pyrrole ring; these rings are shared by two adjoining units. In the naming of such polymers, it is reasonable to employ the name of the connecting ring¶—for example, polyphthalo-(V) and (VI), polynaphthalo-, polythiopheno-(VII), and polyfurano-cyanines (VIII)[14-16].



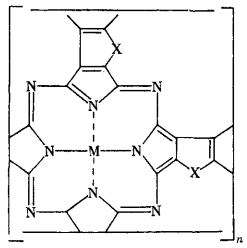
(V)



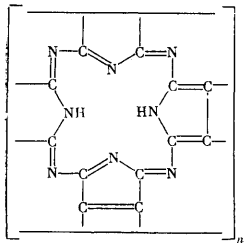
(VI)

The PA whose elementary units are linked directly by the pyrrole rings of the azaporphin in the 3- and 4-positions, for example, the polymers of tetracyano-ethylene[17,18], (IX) and (X), the copolymers of azaporphin with the nitrile of maleic acid, phthalonitrile (XI), etc.[19] should be included in the same group.

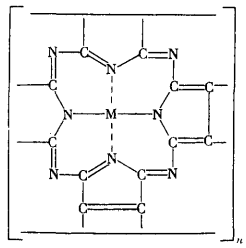
A distinctive feature of the PA of this group is the presence of a continuous conjugation chain throughout the macromolecule regardless of whether these polymers have ribbon [compounds (VI) and (XI)] or planar-network [compounds (V), (VII), and (X)] structures.



(VII) X = S;
(VIII) X = O

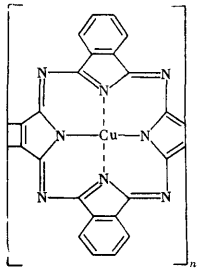


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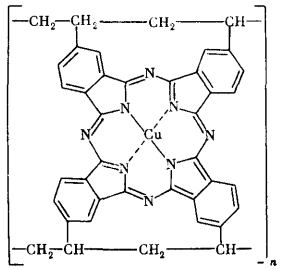


(X)

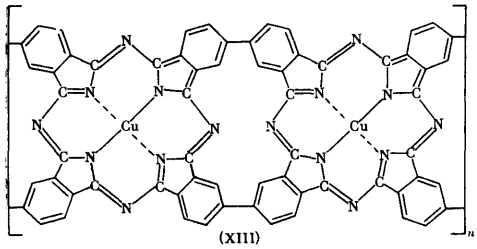
In the macromolecule of a PA belonging to the second group each aromatic (or heteroaromatic) ring linking up the azaporphin is associated with only one unit. In certain cases these rings can be linked in the macromolecule by various bridging groups, such as –O–, –S(O)–, –NH–C(O)–$(CH_2)_{n-2}$–, –C(O)–NH–, etc. The PA of the second group include polymers obtained by the interaction of *N*,*N*′-bis-(3,4-dicyanophenyl)alkylenediamines with metals or their salts[20], of bis-(3,4-dicarboxyphenyl) sulphone with copper[21], of 3,4-dichlorostyrene with copper cyanide [compound (XII)][2], of 3,3′,4,4′-tetracyanobiphenyl with copper [compound (XIII)][2], and of 2,3-dicyanohydroquinone with metal salts or oxides[22], as well as the copolymers of phthalic anhydride and bis(dicarboxyphenyl) ether [compound (XIV)][23], of phthalonitrile and bis(dicarboxyphenyl) sulphone[24], etc.



(XI)

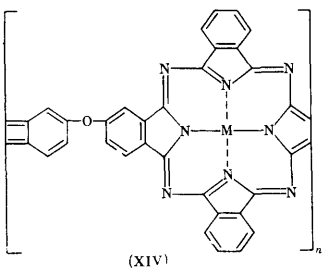


(XII)



(XIII)

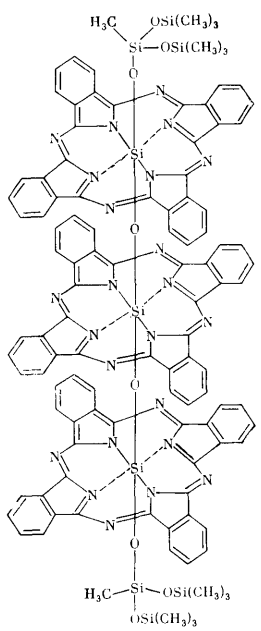
¶For a different nomenclature of the PA, see Smith[13].



(XIV)

The degree of delocalisation of π electrons and the type of conjugation of the PA of this group are various and are determined by the nature of the bridging groups. Together with the PA in which the conjugation between the units is almost unaffected or is only slightly affected, polymers are known with saturated bonds in the macromolecular chain where the azaporphin macrorings are present only at the ends of the chain[25] or exist in the form of individual fragments separated from one another by considerable distances[20,26-29]. However, even when azaporphin rings are only occasionally incorporated in the macromolecular chain, they alter the properties of the latter significantly. Polymers with such rings exhibit an enhanced electrical conductivity and thermal and chemical stabilities, which makes it possible to employ them as special binders, coatings, and adhesives[20,28,29].

Finally, the third group comprises PA whose individual units are joined by oxygen atoms linked directly to the metal atoms of two neighbouring rings[30-32]. These are PPC_{Ge}, PPC_{Si} (XV), etc., obtained by the interaction of the derivatives of the corresponding phthalocyanines. A distinctive feature of these polymers is the fact that the individual units are located in parallel planes and are joined to one another via -O-M-O- bridges, forming in space unusual stacks of rings.



(XV)

The above systematic arrangement is to a large extent arbitrary, requiring further improvement. Nevertheless, it can assist in a better understanding of the large class of PA and facilitates the comparison of the properties and the determination of the specific features of the polymers in each group.

Polymers have been obtained recently whose macrorings constitute a kind of modification of azaporphin: one or several pyrrole rings of the latter have been replaced by pyridine, pyrazine, or other heterocycles[33-35]. Owing to the insufficiency of experimental data, these polymers as well as other structural analogues of PA (polyporphyrins)[36] are not considered in this review; for the same reason, very little space has been devoted to the PA of the second and third groups.

This review presents a survey of the results of studies on the synthesis and certain properties of polymers with a continuous conjugation system whose macromolecules consist of repeating azaporphin macrocycles (PA belonging to the first group), carried out during the last 15–18 years.

II. PRINCIPAL METHODS OF SYNTHESIS

The majority of the PA known hitherto are oligomeric compounds in which the number of units varies from three to six–seven, i.e. having a molecular weight of 1500–5000[39,40]. For certain PA, the degree of polymerisation is 11 and even 14†.[39] According to Berezin and Shlyapova[39], the degree of polymerisation of metal-containing polyphthalocyanines depends on the nature of the metal. In the case of metals with a sterically strained coordination (Ru, Os, and Mo) it is lower than for metals whose coordination does not involve a distortion of the ligand field (for example, Cu, Ga, and Zn).

Metal-containing PA are obtained by the polycyclotetramerisation of tetrafunctional derivatives of aliphatic or aromatic acids having a suitable structure with metals or their oxides and salts. Pyromellitic acid tetranitrile[41] and dianhydride[42], diphthalyl ketone[43], tetracyanoethylene[19], 2,3,4,5-tetracyanothiophen, 2,3,4,5-tetracyanofuran, bis-(3,4-dicarboxyphenyl) ether[44], bis-(3,4-dicyanophenyl) ether[16], etc. are used as the initial compounds in this reaction. In the synthesis of PA having a ribbon structure, the above monomers are sometimes copolymerised with bifunctional compounds such as phthalonitrile, maleic acid dinitrile, etc.

The polycyclotetramerisation process accompanying the formation of the PA is frequently referred to as the "phthalocyanine synthesis" and is carried out similarly to the synthesis of low-molecular-weight porphyrazine complexes. The initial reactants are heated to a temperature from 100° to 300–350°C in solution (in nitrobenzene, ethylene glycol, cyclohexanone, biphenyl, etc.) or in the monomer melt for 10–20 h. The reaction catalysts are ammonia, urea, ammonium molybdate, etc., which in many instances not only accelerate the process but are also involved in the formation of the final products. Low-molecular-weight admixtures are extracted with acetone, alcohol, and benzene, depending on the nature of the starting materials and are also eliminated by vacuum heat

† Although various methods for the determination of the molecular weights of PA have been mentioned in the literature (spectroscopic[39], potentiometric titration of end groups[39,40] etc.), none of them yield exact information about the molecular weight of the polymers. The data obtained with the aid of these methods must be regarded as highly approximate.

treatment at 190–250°C and a residual pressure of 10^{-3}–10^{-5} mmHg. In order to remove traces of inorganic impurities (metals and their salts which failed to react, residues of inorganic catalysts, and their reaction products), the final products are subjected to an acid treatment. The choice of acid and of the conditions of this treatment depend on the type of complex-forming agent. Similarly, using mixtures of various metal salts, one can obtain di-, tri-, and poly-metallic complexes of PA with two and more different metals in the macromolecule[16,45].

The polycyclotetramerisation of the above compounds in the absence of metals leads to metal-free PA.[46,47] The latter are also obtained by the acid treatment of PA_{Na}, PA_{Ca}, etc.[42,48] (see Section IV).

When the "phthalocyanine synthesis" is used, the following factors should be taken into account.

1. The structure of the PA obtained in this way is as a rule inhomogeneous with respect to its chemical composition and contains an appreciable proportion of different defects. These include uncyclised sections of the macromolecule, intermediates attached to the chain, and residual amounts of the solvent and low-molecular-weight compounds firmly linked to the polymer. The higher the chemical reactivity of the monomer, i.e. the greater the tendency of the monomer to undergo various types of reactions in the course of polymerisation, the more defects are to be expected in the structure of its polymers under these conditions. Indeed, comparative study of the polymers obtained from tetracyanoethylene and tetracyanobenzene showed that the structure of the former is much more defective‡.

Copolymerisation of chemically reactive and relatively inactive monomers leads to the formation of copolymers with a more homogeneous chemical composition compared with the corresponding homopolymers (for example, the structures of the tetracyanoethylene–phthalonitrile of tetracyanoethylene–tetracyanobenzene copolymeric copper complexes are much more homogeneous with respect to chemical composition than that of $PTCE_{Cu}$[52]).

2. The use of ammonium molybdate as the reaction catalyst[53–55] leads to the formation of molybdenyl-phthalocyanine together with the main product[56]. Although PPC_{MoO_2} decomposes on prolonged treatment with concentrated H_2SO_4, the use of this catalyst complicates the isolation of the final products and contaminates them.

3. The acid purification of the PA synthesised is accompanied by the hydrolysis of the free groups of the polymer [terminal and surrounding ("framing") groups] and of various intermediates formed in the course of the synthesis, which increases the chemical inhomogeneity of the system to a still greater extent.

The inhomogeneity of the structure of the PA obtained by "phthalocyanine synthesis" is reflected significantly in their properties and hinders a comparative study of the properties of the PA complexes of different metals, particularly those synthesised by different workers. In this connection the series of critical comments by Boston and Bailar[14] concerning the work of Inoue et al.[45] apparently requires additional careful tests.

In order to reduce the defectiveness of the structure and to increase the degree of its homogeneity with respect to chemical composition, polymers are subjected to a prolonged vacuum heat treatment. This involves the splitting off of free functional groups and the removal of the residues of the solvent, monomer, and low-molecular-weight intermediates with simultaneous cross-linking and additional cyclisation, which leads to an increase of the regions of continuous conjugation and of the molecular weight of the specimen.[57–60] The latter is confirmed, in particular, by the change in the nature of the absorption spectrum of the heat-treated polymer relative to the initial specimen. The spectrum of the treated polymer is less steep, apparently owing to the increase of the absorption in the long-wavelength region due to the larger molecules formed on cross-linking[61]. The vacuum heat treatment can be accompanied by a change in the crystal lattice parameters of the PPC or the conversion of their structure into an amorphous form. As a rule, polymers lose their solubility and ability to be pressed after heat treatment.

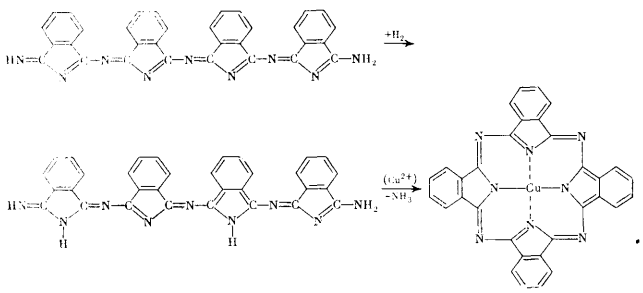
The most effective way of increasing the chemical homogeneity of the structure involves polymerisation in the monomer vapour, developed in 1958–1960 in relation to the synthesis of polymeric tetracyanoethylene complexes[17,19]. Subsequently it was used to obtain also other PA. In order to obtain PA by this method, powders, films, or other types of solid metallic or non-metallic materials are heated in the vapour of the corresponding monomer in the presence of small amounts of moisture, ammonia, or other initiators. The reaction proceeds on the surface with formation of both metal-containing and metal-free PA in the form of films of any size and with any profile, depending on the form of the supports used. This method is free from many of the disadvantages of the usual "phthalocyanine synthesis". It does not require the application of acids, alkalies, or solvents, which promotes the formation of products with a more homogeneous chemical composition. When the reaction is carried out in the monomer vapour, the polymers are obtained in the form of film coatings, which eliminates the necessity for reprocessing, greatly facilitates the investigation, and leads to practical applications of the PA.

Despite the many years which have elapsed since the synthesis of the first porphyrazines§, the mechanism of their formation has been inadequately investigated. It is only known that transition from aromatic dinitriles, *o*-arylenedicarboxylic acids and their anhydrides and imides to phthalocyanines proceeds via 3-aminoiminoisoindolenine, a series of transformations of which leads to the azaporphin[62]. The final reaction stage has come to be

‡ The electron affinity of tetracyanoethylene is much greater than that of tetracyanobenzene [it amounts to 1.6–1.8 (Brieglebe[49]) or 2.8 (Batley and Lyene[50]) compared with 0.4 eV for tetracyanobenzene[51]] and the compound exhibits an exceptionally high chemical reactivity in substitution, Diels–Alder, oxidation-reduction, etc. reactions.

§ Phthalocyanines were discovered accidentally in 1928 and soon (1929–1930) systematic studies on these compounds were begun. The phthalocyanine dimer was obtained in 1949. The first publications on the synthesis of PA appeared in 1958–1959[15,17,18,23,40].

represented by the following scheme:



The replacement of bifunctional acids by tetrafunctional acids greatly complicates the reaction. Polycyclotetramerisation is determined to a greater extent than the formation of phthalocyanines by the nature of the initial reactants, particularly in its first stages. Thus it has been shown that the polycyclotetramerisation of tetracyanoethylene proceeds via the radical-anions of this monomer, the rate of formation of which parallels the rate of formation of the polymer[64,65]. Polyphthalocyanines are apparently synthesised via pyromellitic acid diimidine, which was detected in the interaction of tetracyanobenzene with ammonia and served as the starting material for the synthesis of PPC and PPC_{Cu}.[66] It is quite likely that pyromellitic acid diimidine plays the same role in the polycyclotetramerisation reactions as that of 3-aminoiminoisoindolenine in the synthesis of PC.

The study of the formation of PPC from tetracyanobenzene showed that oligomeric porphyrazines, soluble in organic solvents, are formed in the initial stages and are subsequently converted in the course of the reaction into insoluble planar cross-linked polymers. It is then unimportant whether the reaction takes place in the melt or in a monomer solution. In our view, the reported synthesis[47] of insoluble PPC did not involve polymerisation in solution at all, as stated erroneously by Radyushkina et al.,[67] but was associated with the nature of the solvent (formamide) employed in the reaction, which in this case behaves as a cross-linking agent. It has been shown that the polymerisation of tetracyanobenzene in the presence of specific amounts of the initiator leads to PPC which are believed to have a ribbon structure and are soluble in organic solvents.

The transition to insoluble PPC with a planar cross-linked structure takes place gradually and is faster the higher the reaction temperature and the greater amount of the initiator introduced into the system. An increase of pressure in the reaction mixture apparently has a similar influence on the rate of transition[68].

The formation of metal-substituted PA is accompanied in addition by oxidation-reduction reactions. This is indicated by the presence of the heterovalent Fe^{3+} and Fe^{2+} ions in the PPC_{Fe} molecules obtained by the interaction of tetracyanobenzene with $FeCl_3$.[69] The polycyclotetramerisation of tetracyanoethylene under analogous conditions leads to $PTCE_{Fe}$ with Fe^{3+} in the macroring and with Fe^{2+} in radical-ion salts, which are apparently located at the end of the macromolecule[69,70].

The method of "phthalocyanine synthesis" has been inadequately investigated. Nevertheless, this is the principal, widely used procedure for the synthesis of PA. Only a few types of PA among those investigated hitherto have been obtained by other methods. Germanium- and silicon-polyphthalocyanines having a "loop" structure have been synthesised by the interaction of derivatives of the corresponding phthalocyanines[30-32]. When PC_{Cu} was fused with sulphur, P_4S_{10}, or SCl_2 at 460°C, the products were PPC_{Cu} with sulphide bridges in the macromolecule[71]. New polyamides with azaporphin macrorings have been obtained by the condensation polymerisation of phthalocyanines, containing functional groups, with various diamines[26].

The synthesis of metal-substituted PA by treating the corresponding metal-free polymers with metal salts merits particular attention[19,70]. This method makes it possible to obtain the PA complexes of various metals under comparable conditions. With its aid, it has been possible to obtain for the first time and to separate the univalent complexes of PPC_{Fe} with bivalent and tervalent iron in the macroring[69,70]. The homogeneity of the structure is specified in this case by the initial metal-free polymer and does not undergo any appreciable changes on treatment with metal salts.

A more detailed development of methods specific to polymeric compounds, different from the method of "phthalocyanine synthesis", will lead in the future to new procedures for the formation of PA.

III. THE STUDY OF STRUCTURE

The structure of PA is studied mainly in order to detect azaporphin macrorings in the macromolecules synthesised. For this purpose, one uses as a rule elemental and spectroscopic analyses. However, this is difficult owing to the insolubility and infusibility of the majority of PA; the most reliable results have been obtained only for the soluble fractions of the polymers.

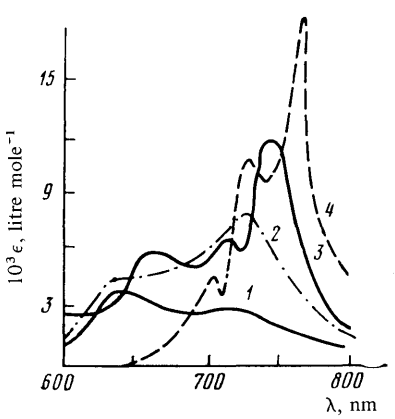


Figure 1. Electronic absorption spectra of PPC; solvents: 1) acetone; 2) dimethylacetamide; 3) concentrated H_2SO_4; 4) PC in concentrated H_2SO_4.

The azaporphin structure of the polymers synthesised has been confirmed by the presence in the spectra of these polymers of bands which are usually attributed to the azaporphin "skeleton". The infrared bands at 745–750, 810–885, 945–950, 1045–1060, 1080–1090, and 1118–1123 cm^{-1} correspond to the vibrations of the "skeleton"[72]; in the electronic absorption spectra there is a long-wavelength band in the range 600–800 nm.

Agreement between the spectra of the polymers and the corresponding low-molecular weight analogues is observed for all types of PA, both metal-free and metal-substituted, regardless of the nature of the metal and the molecular weight of the PA. The nature of the spectra depends significantly on that of the solvent employed (Fig. 1) for both PA and various derivatives of low-molecular-weight porphyrazines[73,74].

Recently published communications[69,75,76] concerning the studies of iron-phthalocyanines by Mössbauer spectroscopy report the development of a new extremely effective method for the investigation and identification of the structures of azaporphin complexes, including insoluble planar cross-linked complexes. The use of this method made it possible for the first time to carry out a comparative investigation of soluble and insoluble PA, to compare data for different types of PA, and to elucidate the influence of the conditions of synthesis and treatment on the structure of the polymers obtained. The study of the Mössbauer spectra of PC_{Fe}, soluble and insoluble PPC_{Fe}, obtained both by "phthalocyanine synthesis" (in solution, in the melt, and in the monomer vapour) and from PPC, as well as $PTCE_{Fe}$ revealed a fairly satisfactory agreement between their isomeric shifts (δI) and quadrupole splittings (ΔE). This indicates the presence in the structures of all the complexes of ligands having the same electronic structure[69,70]. Consequently all the polymers investigated have a structure analogous to that of PC_{Fe}, i.e. they contain azaporphin macrorings.

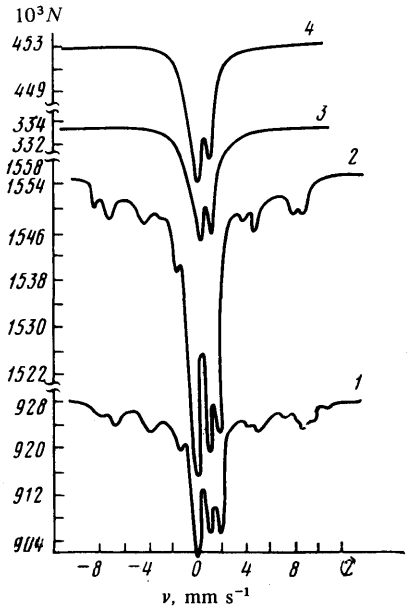


Figure 2. The Mössbauer spectra recorded at different temperatures for PPC_{Fe} obtained by the introduction of iron into PPC; temperature (K): 1) 2; 2) 4.2; 3) 90; 4) 300; v = speed of the source relative to the absorber; N = quantity proportional to the number of pulses.

It is noteworthy that hitherto there has been no unanimous view in the literature concerning the structures of polymeric tetracyanoethylene derivatives, because it is impossible to obtain reliable spectra of these polymers owing to their poor solubility. Their azaporphin structure was confirmed only by the results of elemental and chemical analyses[19,60,77]. However, there have been studies[78] in which a different structure was attributed to polymeric tetracyanoethylene derivatives. The agreement between the values of ΔE and δI for the Mössbauer spectra of $PTCE_{Fe}$, PC_{Fe}, and PPC_{Fe} constituted a convincing confirmation of the azaporphin structure of the given class of polymers.

The application of Mössbauer spectroscopy also made it possible to determine the valence of the metal in the polymeric iron-azaporphins and to elucidate the conditions for the formation of PPC_{Fe} with the metal having a particular valence[69,70].

As for PC_{Fe},[75,76] the values of $E\theta$ and δI for PA_{Fe} depend only slightly on temperature and the metal content or not at all. The study of PPC_{Fe} with different metal contents in the macromolecule[70] at 4.2 and 2 K revealed a hyperfine structure of the Mössbauer spectroscopic lines (Fig. 2), which indicates the operation of a powerful spin–spin mechanism of the relaxation of the electronic spin of Fe^{3+}. This suggests in its turn the occurrence in such systems of an exchange magnetic dipole interaction between the iron ions in the macromolecules.

A wider employment of Mössbauer spectroscopy will throw light in the future on many hitherto obscure problems concerning not only the structure but also the mechanism of the formation of PA.

IV. CERTAIN PHYSICOCHEMICAL, ELECTRICAL, AND CATALYTIC PROPERTIES

1. Physicochemical Properties

Polyazaporphins are infusible thermally stable dark-coloured compounds whose colour ranges from blue-green to black. Depending on the method of synthesis and the conditions in the subsequent treatment, they can be obtained in the amorphous and fully crystalline forms[16,68,79]. The thermal stability of the PA is determined by its chemical structure and the degree of its homogeneity, the nature and number of free functional groups, and the nature of the metal in the macroring. Unfortunately the available literature data do not allow a complete analysis and survey of the characteristics of the thermal stabilities of such systems. One can only reach a conclusion (and even that only very approximately) about the temperature to which PA may be heated without appreciable decomposition. Thus diphthalyl ketone polymers withstand heating to 450°C[43] and certain specimens of polymeric tetracyanoethylene derivatives are stable in air up to 300–350°C and in an inert atmosphere up to 500–550°C.[57]

On the other hand, polymeric tetracyanothiophen and tetracyanofuran derivatives decompose in air below 300°C.[16] The comparatively low stability of the latter is apparently associated with the presence of acetylacetonato-groups in their structure. The presence of such groups together with a variable-valence metal creates favourable conditions for the formation of peroxy-radicals capable of initiating the decomposition of the polymer, which has been demonstrated in the study of the thermal stabilities of $PTCE_{Cu}$, $PTCE_{Fe}$, etc.[57] In those cases where it was

possible to eliminate these groups from the structure, the stability of the polymers increased appreciably. The increase of the chemical homogeneity of PA also promotes an increase of their thermal stability regardless of whether such homogeneity is obtained by the alteration of the conditions of synthesis or in the course of an additional treatment of the specimen[57].

Comparative study of the thermo-oxidative degradation of PC_{Co} and its polymeric analogue, on the one hand, and metal-free and metal-substituted PA, on the other, revealed a lower rate of thermolysis of PPC_{Co}, while the other reaction parameters remained unchanged[80], and a higher stability in air of metal-free polymers relative to PPC_{Cu} and PPC_{Fe}. The reduced stability of complexes of variable-valence metals on heating in air is associated with the fact that copper, iron, and other variable-valence metals are excellent initiators of the formation of peroxy-radicals (this is well known), which promote in their turn the degradation of the polymers. The stability series is based on their resistance to thermo-oxidative degradation, found for polymeric tetracyanoethylene complexes:[19] $PTCE > PTCE_{Mg} > PTCE_{Cu} > PTCE_{Fe}$; this series can apparently be repeated also for other PA.

The solubility of PA depends on the configuration of the chain and the "frame" surrounding the azaporphin macrorings. While planar cross-linked polyphthalocyanines, referred to as poly(tetramethineporphyrazines) by Akopov[13], do not dissolve in organic solvents, ribbon polyphthalocyanines [Akopov calls them poly(dimethinedibenzoporphyrazines)] partly dissolve in dimethylformamide, dimethylacetamide, and pyridine. Their solubility is higher the greater the number of end groups forming the "frame" in the macromolecule. A large number of functional groups in polymer macromolecules as well as bulky substituents in the molecules of low-molecular-weight porphyrazines[81,82] prevent the close packing of such systems, which increases their solubility.

Oligomeric PPC with a large number of surrounding ("framing") nitrile groups, which are soluble in acetone, have been obtained recently; poly(disulphonephthalocyanine), obtained from PA-bis(3,4-dicarboxyphenyl) sulphone, is soluble in water[24].

Despite the fact that the basicity of the azaporphin compounds is greatly reduced owing to the involvement of the free electron pairs of the peripheral nitrogen atoms in the construction of the metal-like molecule, a characteristic feature of these compounds is their solubility in concentrated H_2SO_4, the dissolution being accompanied by the protonation of the macromolecule[23]. The solubility of the PA in the acid is lower than the solubility of their low-molecular-weight analogues and depends on the structure of the polymer and on the nature of the central metal atom. Thus, in contrast to the ribbon PA, which are readily soluble in acid, the planar cross-linked PA dissolve in concentrated H_2SO_4 only after prolonged (up to 5–6 days) treatment. The solubility of metal-containing PA in concentrated H_2SO_4 is higher the more pronounced the electron-donating properties of the metal atom in the "window" of the macroring.

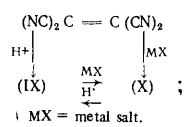
The resistance of PA to acid is determined by the configuration of the polymer chain and the nature of the central metal atom in the ring. As a rule, the PA of the first group (the section I) are less stable in acid than their low-molecular-weight analogues. Thus the stability of PC_{Zn} in acid is approximately 10 times greater than that of PPC_{Zn},[84] and the rate constant for the degradation of PC_{Co} in H_2SO_4 at 25°C is smaller by three orders of magnitude than for PPC_{Co}.[85] The resistance of silicon complexes to acid is also considerably inferior to that of their low-molecular-weight analogues, although the PPC_{Si} of the third group, having a "loop" structure, are much more stable in acid than PC_{Si}.[86,87]

Depending on the nature of the central metal atom, the PA as well as phthalocyanines[88] can apparently be divided into two groups in terms of their resistance to the action of concentrated H_2SO_4: stable PA which do not undergo an appreciable change when treated with the acid and labile complexes which lose the metal after the acid treatment and are converted into the metal-free polymers. In terms of the degree of elimination of the metal from the macroring, which is inversely proportional to the strength of the M–N interaction, metals can be arranged in the following sequence[26]:

$$Zn^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} \gg Cu^{2+} \quad .$$

The ability of the PA complexes of sodium, magnesium, calcium, etc. to lose the metal in the course of the acid treatment has found an application, as already stated, in the synthesis of metal-free PA. The ability of metal-free porphyrazines to interact with metals or their salts on heating is used to synthesise metal-substituted azaporphin complexes[89]. The reaction is carried out both in solutions[19,70] and in suspensions, the polymer powder being treated with a solution of the salt[90,91].

Thus PA as well as their low-molecular-weight analogues are a kind of molecular sieve which absorb and, under appropriate conditions, give up metal ions. In other words, they are capable of undergoing the polymer complex–metal-free polymer transition, illustrated schematically below for polymeric tetracyanoethylene derivatives[18]:



This property of polyazaporphins may lead in the future to their utilisation as complex-forming ion exchangers and organic molecular sieves operating at elevated temperatures.

2. Electrical Properties

The electrical properties of PA, whose study was begun in 1959–1960,[41,92] have been frequently discussed in connection with the consideration of the properties of organic semiconductors[93–95]. We shall therefore deal below only with questions which have not been adequately dealt with in the above monographs.

The specific conductances σ of polyazaporphins are higher by several orders of magnitude than for their low-molecular-weight analogues and the activation energies for electrical conduction E in the polymers are much lower (see Table). The dependence of E on the medium in which the measurements are made has been observed for a whole series of complexes (it is more pronounced in nitrogen and less so in ammonia than in air[16]) and E has been found to vary in parallel with the optical excitation energy (see Table).

The conductivity of $PTCE_{Cu}$ films obtained in monomer vapour has been found to be anisotropic: σ is greater by 3–7 orders of magnitude parallel to the film surface than in the perpendicular direction. The dielectric constants and σ of PA vary exponentially not only with temperature

but also with pressure. The linear decrease of the resistivities ρ with increase in pressure has been attributed to the increase of the intermolecular overlap, which facilitates charge transfer in the case of closer-packed polymer chains and layers [99].

One of the important problems in the study of the electrical properties of porphyrazines is that of the influence of the nature of the central metal atom and of the ligand on the electrophysical parameters. Many investigators have explained the slight decrease of E after the introduction of the metal into the PC by the fact that the conductivity of such systems is determined exclusively by the π electrons of the conjugated system of the macroring. Furthermore, the mobility of the current carriers μ depends on the degree of overlap of the metal and macroring orbitals. The greater the overlap, the higher the value of μ [thus $\mu(PC_{Ag}) > \mu(PC_{Cu})$], [100] so that the conductivity of the system should also be higher ($\sigma = en\mu$, where n is the concentration of current carriers). Indeed σ and E for polymeric tetracyanoethylene complexes of a number of metals are different and also differ from the analogous parameters of the metal-free polymer. For example E = 0.53, 0.32, and 0.18 eV have been obtained for PTCE, $PTCE_{Cu}$, and $PTCE_{Ag}$ respectively [101]¶.

The electrophysical parameters and the positions of the longest-wavelength absorption maximum for certain azaporphin compounds.

No.	Specimen*	σ_{300}, Ω^{-1} cm^{-1}	σ_0, Ω^{-1} cm^{-1}	E, eV	λ_{max}, nm	Refs.
1	β-PC_{Cu}	$1.9\cdot10^{-14}$	$1.2\cdot10^{3}$	1.95	—	71
2	PC_{Cu} dimer	—	—	1.0–0.7	—	12
3	PPC_{Cu}	$5.9\cdot10^{-6}$	$1.6\cdot10^{-2}$	0.41	750	71
4	$PPC^{**,***}_{Cu}$	$2.3\cdot10^{-2}$	—	0.15	—	97
5	$PTTPC^{**}_{Cu}$	$3\cdot10^{-7}$	$2\cdot10^{-3}$	0.45	—	96
6	$PThiC^{**,***}_{Cu}$	$5.5\cdot10^{-5}$	$1.0\cdot10^{-1}$	0.36	—	96
7	$PThiC^{**}_{Cu}$	$3.3\cdot10^{-12}$	$5.8\cdot10^{-7}$	0.62	—	16
8	$PThiC^{**}_{Cu}$-Ni	$8\cdot10^{-6}$	$1.3\cdot10^{-2}$	0.37	—	16
9	$PThiC^{**}_{Cu}$-Mg	$6.8\cdot10^{-7}$	$5.6\cdot10^{-4}$	0.36	—	16
10	$PTCE^{**,***}_{Cu}$	$18\cdot10^{-7}$	—	0.50	—	97
11	$PTCE_{Cu}$	10^{-5}	$10^{-0.4}$	0.32	—	19
12	$PTCE^{***}_{Cu}$	10^{-2}	10	0.18–0.1	—	19
13	Chloro-PC_{Zr}	$2.0\cdot10^{-10}$	$2\cdot10^{2}$	1.43	693	98
14	PPC_{Zr}	$2.2\cdot10^{-7}$	$8.8\cdot10^{-2}$	0.54	746	98
15	PPC_{Sc}	$4.3\cdot10^{-8}$	$1.42\cdot10^{-3}$	0.53	750	98
16	PPC_{Co}	$3.2\cdot10^{-9}$	$6.22\cdot10^{-4}$	0.62	726	98

*All the specimens except Nos. 7, 11, and 12 were synthesised in melts of the initial reactants. Specimen No. 7 was obtained in solution in cyclohexanol and specimens Nos. 11 and 12 were synthesised in tetracyanoethylene vapour.

**The polymers were obtained by the interaction of the corresponding tetranitriles with metal acetylacetonates.

***The specimens were subjected to a preliminary heat treatment at 200–300°C.

¶For polymers obtained in the monomer vapour.

The dependence of the electrophysical parameters on the nature of the central metal atom is manifested also in the study of bimetallic PA [16,102] (see Table). An attempt has been made [16] to compare the experimental values of σ for the polymeric tetracyanothiophen complexes of various metals with the ionic radii and ionisation potentials (Fig. 3) of their cations.

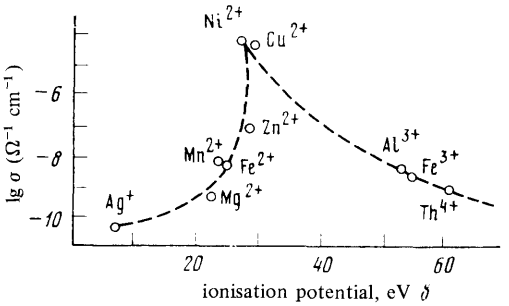


Figure 3. Dependence of the electrical conductivity of the polythiophenocyanine complexes of a number of metals on the ionisation potentials of the cations.

The fact that the maximum values of σ have been observed for PA containing metals whose cationic radius is approximately 0.75 Å is striking. If account is taken of the fact that the cations having such a radius can be accommodated most favourably in the "window" of the azaporphin macroring [103], the influence of the degree of overlap of the electronic orbitals of the metal and the ring on the conductivity of such systems becomes evident: the most complete overlap of the electronic orbitals of the metal and the ring leads to an increase of μ and hence also σ.

Analogous relations have been obtained also for polytetrathiafulvalenocyanines (PTTFC) [96]. The observed relations give rise to the following sequence of metal cations arranged in terms of decreasing electrical conductivities of their polyporphyrazine complexes:

$$Ni^{2+} > Co^{2+},\ Cu^{2+} > VO^{2+},\ Mn^{2+},\ Zn^{2+} > VO_2^{2+},\ Cr^{3+},\ Fe^{3+} > Mg^{2+}$$

Comparison of the electrophysical properties of various PA_{Cu} also revealed the influence of the nature of the ligand on σ and E. It was observed that E decreases in parallel with the decrease of the aromaticity of the rings connecting the azaporphin macrorings into a polymer chain—from benzene, via thiophen, to furan, i.e. in the sequence $PPC_{Cu} > PThiC_{Cu} > PFuC_{Cu}$, where $PFuC_{Cu}$ is the polymeric copper complex of tetracyanofuran and $PThiC_{Cu}$ is the polymeric copper complex of tetracyanothiophen [16].

We do not believe it is possible to arrive at more far-reaching conclusions about the influence of the nature of the ligand and the metal on the electrophysical properties of PA, because, despite the extensive experimental data available, there are no literature data on the purities and homogeneities of the structures of the given polymers. Frequently there is no description of the nature of the preliminary treatment of the specimens. At the same time, the Table shows that the change in the conditions of the synthesis (cf. specimens Nos. 6 and 7 and Nos. 10 and 11)

and additional heat treatment of (Nos. 11 and 12) have a significant influence on the electrophysical parameters of PA.

Numerous experiments have shown that an increase of the duration of the synthesis, additional vacuum heat treatment of the polymers, polymerisation in the monomer vapour, as well as copolymerisation with chemically inactive monomers promote the formation of more homogeneous and sometimes more ordered structures with an enhanced electrical conductivity (see Table). In this connection we may mention that the method of synthesis of metal-substituted PA with the aid of metal acetylacetonates, previously proposed by the present authors [79], does not appear to us to be altogether successful at the present time. Indeed, the polymers obtained by this method contain acetylacetonato-end groups (which frequently also make up the "frame") and these as a rule impair many of the properties of PA (see Section IV). Furthermore, and this is the most important factor, in the course of the above reaction appreciable numbers of insoluble side products are formed and are difficult to separate from the main bulk of the polymer, remaining in the specimen as impurities.

This makes the reaction of acid tetranitriles with metal acetylacetonates unsuitable for the synthesis of PA on a preparative scale, particularly when the aim is to discover the relation between the chemical structure and the properties of the polymers.

In order to investigate the mechanism of conduction in semiconductors, one usually determines the temperature variation of n, μ, thermo-e.m.f. (α), etc. Measurements of thermo-electromotive forces showed that the PA known at the present time exhibit different types of conductivity. Copper- and zinc-polytetrathiafulvalenocyanines exhibit p-type conductivity [96], while heat-treated films of the polymeric tetracyanoethylene complexes of various metals show n-type conductivity [104]. Electronic conductivity has been observed for scandium-, zirconium-, and cobalt-polyphthalocyanines. Over the entire experimental temperature range, the sign of the current carriers remains unchanged [98]. Sulphur-containing PPC_{Cu} specimens, synthesised from PC_{Cu}, exhibited p-type conductivity, whereas polymers obtained from tetracyanobenzene and subjected to a special treatment with sulphur showed n-type conductivity [71].

A change in the sign of the majority current carriers has been observed for the $PTCE_{Fe}$–metallic iron and $PTCE_{Ag}$–metallic silver compositions as a function of the conditions of the preparation of the system. The compositions obtained were converted in the course of 10–14 h into systems with hole conductivity, the sign of the current carriers changing with increase of the reaction time to 15–20 h [105]. The values of α for a number of PA are 50–70 $\mu V\ K^{-1}$. [96,104]

The mechanism of conduction has been studied in greatest detail for PPC_{Cu}. [106] In the study of the conductivity of this polymer, both positive and negative current carriers were detected, their concentration being almost independent of temperature, while α varied exponentially with temperature. This enabled the authors [106] to conclude that the migration of the current carriers in PPC_{Cu} is an activated process. Although the signs of the majority carriers in PPC_{Cu} and PC_{Cu} were the same, μ for the polymer proved to be smaller than for its low-molecular-weight analogue†. Extrapolation of the measured mobility to an "infinite" temperature, at which there is no hindrance to the migration of current carriers at the breaks in conjugation, leads to $\mu_\infty = 1.4\ cm^2\ V^{-1}\ s^{-1}$.

The results suggest that the comparatively high value of σ in such substances is associated with the high concentration of current carriers whose mobility is low and varies exponentially with temperature. On the basis of an estimate of the concentration of current carriers (10^{18}–10^{19} cm^{-3}), the authors of this investigation believe that the required concentrations of the impurities in polymers resembling those investigated must be reduced at least by 5–6 orders of magnitude compared with inorganic semiconductors.

The Hall effect was measured after frequent unsuccessful attempts only in one study [41]. The authors [41] observed two states for PPC_{Cu}: one state has $E = 0.26$ eV and $n = 10^{16}\ cm^{-3}$, n being independent of temperature, and the other (heat-treated polymer with p-type conductivity) has $n = 10^{18}\ cm^{-3}$, which remains constant within the limits of the measured temperatures. However, these results were not subsequently confirmed‡. Having estimated the sensitivity of the apparatus in which the Hall effect was measured for PPC_{Cu}, the authors [106] concluded that the mobility of the current carriers in the test specimens is not greater than 0.3 $cm^2\ V^{-1}\ s^{-1}$ at 18–250°C. This implies in its turn that the comparatively high electrical conductivity of the specimens (for example, $\sigma_{300} = 10^4\ \Omega^{-1}\ mm^{-1}$) must be due to a high concentration of current carriers, exceeding $2 \times 10^{17}\ cm^{-3}$. [106]

It is now well known that measurements carried out using a direct current cannot yield a unique picture of the conduction mechanism, which apparently involves two processes: the transport of carriers from one continuous conjugation region to another and the conduction within these regions themselves. In order to elucidate the conduction mechanism, measurements must be made of the frequency dependence of the electrical parameters; some of these parameters for polymeric tetracyanoethylene derivatives have been published [93].

The study of the frequency dependence of the dielectric constants and σ as a function of the electric field strength for PPC showed that these polymers are one-dimensional semiconductors in which the conductivity regions extend over 100–1000 Å. [99]

3. Catalytic Properties

The study of the catalytic properties of PA showed that, as in many other organic semiconductors, these compounds exhibit an enhanced activity in relation to oxidation-reduction reactions such as the oxidation of aromatic alkyl-substituted hydrocarbons [109,110] and certain aromatic and saturated aliphatic aldehydes [111], the decomposition of formic acid and hydrogen peroxide [112], etc.

In terms of their reactivity, the polymeric complexes are as a rule superior to their low-molecular-weight analogues. An exception is $PPC_{Os(SO_4)_2}$, whose catalase activity is five times smaller than that of $PC_{Os(SO_4)_2}$ and PPC_{RuHSO_4}, the latter having the same activity as

† According to Heilmeir et al., [107] μ for PC_{Cu} is 0.1–0.4 $cm^2\ V^{-1}\ s^{-1}$.

‡ It is quite likely that the Hall effect cannot be measured at all for PA as well as a whole series of semiconductors with a jump conductivity mechanism [108].

PC_{RuHSO_4}.[113] A characteristic feature of the polymeric complexes as oxidation-reduction catalysts is their appreciably greater selectivity than that of the corresponding low-molecular-weight analogues, reaching 100% in many instances, for example in the dehydrogenation of formic acid, the oxidation of cumene[110], etc.

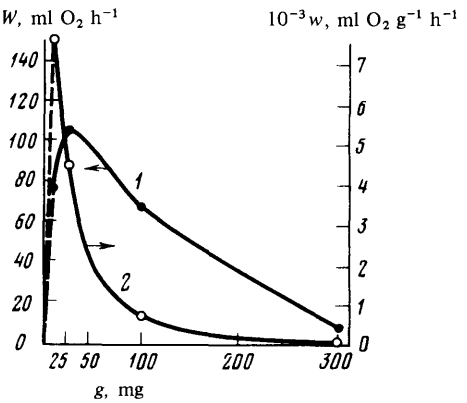


Figure 4. The influence of the amount of PPC_{Fe} on the rate of oxidation of cumene: 1) overall rate of reaction (W) relative to the catalyst sample (g); 2) specific rate of reaction (w) per gramme of catalyst.

Like certain other catalysts, PA exhibits a dual function in reactions. Depending on the amount of PA introduced into the reaction, the complexes behave as both process initiators and inhibitors. This property is illustrated in Fig. 4 in relation to the effect of PPC_{Fe} in the oxidation of cumene.

The problem of the centres which determine the catalytic activity of porphyrazines has not at first sight been solved unambiguously. On the one hand, there is evidence for the decisive influence of the nature of the metal on the catalytic activity of phthalocyanines and, on the other hand, there is evidence showing that the peripheral nitrogen atoms of the macroring play the main role without any participation of the metal. Indeed, while the activity of PPC and PTCE in the oxidation of cumene is insignificant, the complexes of these polymers with iron and copper show a fairly high activity, which depends on the amount of metal in the macromolecule and increases with the latter[110]. However, the introduction of a second metal does not cause an appreciable enhancement of the catalytic properties of PPC_{Cu} in this reaction[110], in contrast to the effect observed by Inoue et al.[102]

The dependence of the catalytic activity on the nature of the metal has been investigated much more extensively for phthalocyanines than for PA and has been demonstrated in relation to various reactions. Thus it has been shown[110] that in the oxidation of cumene the phthalocyanine complexes of variable-valence metals (copper, nickel, and cobalt) exhibit a much higher activity than the phthalocyanine complexes of zinc, mercury, and silver. In formic acid decomposition reactions the specific activity of PC_{Cu} is smaller by more than an order of magnitude than that of PC_{Fe}; in the decomposition of hydrazine the differences between the specific activities of these phthalocyanines exceeded two orders of magnitude, while the addition of PC had almost no influence on this process[114].

It is of interest that even the selectivity of phthalocyanines (but not PA) is related to the nature of the metal. For example, in the oxidation of cumene to its hydroperoxide the phthalocyanine complexes of manganese, iron, cobalt, and nickel are much inferior in their selectivity to the copper and zinc complexes[115].

The finding that PPC_{Fe} obtained without a catalyst is more active in the decomposition of hydrogen peroxide than "the same" complex synthesised in the presence of ammonium molybdate[54] can serve as additional confirmation of the dependence of the catalytic properties of PA on the nature of the metal. The presence in the specimen of admixtures of PPC_{MoO_2}, formed in the catalytic synthesis of PPC_{Fe}, reduced the activity of the latter in the above reaction. This finding shows yet again that catalytic properties as well as electrophysical characteristics must be studied only on carefully purified and chemically homogeneous compounds free from impurities which are not susceptible to analytical determination.

Theoretical calculations, confirmed by experimental data obtained in the study of the electrochemical reduction of oxygen[116,117], showed that the phthalocyanine complexes of metals can be arranged in the following sequence in terms of their decreasing catalytic activities: $PC_{Fe} > PC_{Co} > PC_{Ni} > PC_{Cu}$. Analogous relations have been observed for polymeric complexes. The influence of the nature of the metal on the catalytic activity of phthalocyanines has been observed also in the electrochemical reduction of oxygen on carbon electrodes saturated by the above complexes[67]. The activity series for the phthalocyanine complexes in relation to this reaction, based on the nature of the metal, did not agree with similar series for other reactions[118,119].

However, under certain conditions, there are no differences between the catalytic activities of the phthalocyanine complexes of a number of metals. It has been shown[121] that the catalytic activity of phthalocyanines is determined by the crystal form of the given substances to a greater extent than by the nature of the metal. The observed decrease of the activity of PC_{Cu} in the oxidation of cumene has been explained[122] by the conversion of the catalyst from the α-form into the β-form and the authors concluded that the π-conjugated phthalocyanine system is important.

It has been shown by spectroscopic methods[123,124] that the active centres for the adsorption of organic and inorganic acids can be the nitrogen atoms of the phthalocyanine ring and that the metal atom is not essential for the formation of the phthalocyanine–acid molecule complex. Investigators of polymeric compounds arrived at similar conclusions. Thus it has been shown[125] by kinetic and EPR methods that the active centres for deuterium exchange in PPC_{Cu}, which are active at temperatures above 100°C, arise as a result of the dissociation of double bonds and do not include copper atoms. The authors[125] carried out a thermodynamic estimate, which showed that the chemisorption of hydrogen and hence the catalytic processes involving it are possible on non-metallic centres on organic semiconductors for a width of the forbidden gap below a certain limiting value.

The study of the adsorption of formic acid on PPC_{Cu} by spectroscopic methods at temperatures close to that of the onset of the catalytic reaction demonstrated a decrease of the intensity of the stretching vibration bands of the C–N groups in the infrared spectrum (1090–1310 cm^{-1}) and of the bands in the PPC_{Cu} spectrum in the visible region

(630 and 725 nm) corresponding to the presence of a conjugated system in the polymer. Together with results obtained previously [126,127], these data show that the active centres for the adsorption and dehydrogenation of formic acid in polyphthalocyanines may be the peripheral nitrogen atoms of the azaporphin macrorings of the polymer. The same conclusion follows also from studies of the *para–ortho* transformation of H_2 and deuterium exchange on PPC_{Cu}.[128]

The phthalocyanine activity series in the oxidation of cumene $PC_{RuHSO_4} > PC_{Os(SO_4)_2} > PC_{Co} > PC_{Ni} > PC_{Cu}$ shows, according to Berezin and Shlyapova[129], that the initiation of the reaction is not associated with the interaction of oxygen or the hydroperoxide with the metal in the phthalocyanine complex, since this possibility is altogether lacking in the case of the very active $PC_{Os(SO_4)_2}$.

The above data concerning the nature of the active centres of azaporphin show that the π electrons of the macroring and the *dsp* electrons of the metal constitute a single conjugated system, whose properties depend significantly on the nature of both the ligand and the metal in the "window" of the macroring.

It is of interest that an enhanced activity in oxidation-reduction reactions is manifested only by semiconducting compounds and that polymers (for example, polyphenylene, polyphenylacetylene, etc.) exhibit no such activity whatever in the above reactions, behaving as insulators at the experimental temperatures. This is usually attributed to a correlation between the catalytic and semiconducting properties of compounds of this kind. Indeed, as for many organic semiconductors, it has been noted for PA that the higher the value of σ, the higher the activity of the compound in model reactions[109,110,129,130].

This is manifested particularly clearly when the catalytic activities of PA and their low-molecular-weight analogues are compared. As already mentioned, the electrophysical parameters of the latter are greatly inferior to those of the corresponding polymeric complexes (see Table). This was also observed when the catalytic properties were compared. For example, PPC_{Fe} and PPC_{Cu} exhibit a much higher specific activity in the oxidation of cumene than PC_{Fe} and PC_{Cu} respectively[110]. A similar behaviour has been observed also for the cobalt complexes in the electrochemical reduction of oxygen in the presence of PC_{Co} and its polymeric analogue[67]. In the hydrogen peroxide decomposition reaction the specific activity of PPC_{Cu} is only five times smaller than that of one of the best catalysts for this reaction—manganese dioxide, whereas PC_{Cu} is altogether inactive in this reaction[112]. The specific activities of the phthalocyanine complexes of copper and iron are inferior to those of their polymeric analogues also in the hydrazine decomposition reactions[131].

A correlation between the semiconducting and catalytic properties is also indicated by the parallel variation of the catalytic activity and the concentration of paramagnetic centres, which has been established for certain organic semiconductors[131]. A whole series of chemical reactions involving organic semiconductor catalysts can be accounted for solely in terms of the semiconducting properties of the latter. However, a clear-cut correlation between the electrical and catalytic properties of semiconductors, which might have been expected on the basis of the electronic theory of catalysis on semiconductors[132], is not observed in practice. This led some workers to the conclusion that such a correlation is altogether lacking[133]. For example, the catalytic properties of polychelates have been attributed[134,135] to the electronic state of the metal in the chelate unit and not to the semiconducting properties of these systems. The absence of a correlation between the catalytic and semiconducting properties has also been reported in other studies.

The available literature data do not permit at present any unambiguous conclusions concerning the relation between the semiconducting and catalytic properties. A more detailed investigation of the mechanism of the catalytic action of organic semiconductors together with the study of the mechanism of their conduction and comparison of these data will apparently provide in the future an answer to the question of the fundamental factors influencing the catalytic activity of semiconducting systems. Here one should take into account also other no less significant factors which determine the catalytic activity of semiconductors, namely the local chemical properties of their surfaces, their collective electronic properties, etc.

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In conclusion, one should note that during the last 15–18 years extensive experimental data have been accumulated on the synthesis and properties of polymeric azaporphins, which undoubtedly constitute one of the most striking examples of polymers with a conjugation system. However, the lack of reliable methods for the synthesis and purification of PA has led to a very limited and extremely one-sided study of their properties and only a qualitative interpretation of the experimental data obtained.

Nevertheless, the unusual physical and physicochemical properties observed for these polymers make them valuable objects not only for a wide variety of scientific investigations but also for the creation on their basis of chemically and thermally stable specific catalytic systems as well as special semiconducting materials with a wide range of electrophysical parameters.

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Some Problems of the Chemical Physics of the Ageing and Stabilisation of Polymers

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The ageing and stabilisation of polymers involves the chemical physics of coupled radical-chain, ionic, and molecular transformations in complex multicomponent systems which make up the polymeric material. In the present review the question of the ageing and stabilisation of polymers is formulated as a multifactor problem, where the study of the changes in the properties of the material under various conditions can be treated from a single standpoint, and the mechanism is represented by a set of interrelated elementary processes. Some new results and views are considered.
The bibliography includes 112 references.

CONTENTS

I.	Introduction	1139
II.	The ageing of polymers as a multifactor problem	1140
III.	Characteristics of the chemical reactions in the polymer matrix	1147
IV.	Quantitative characteristics of the elementary stages of the ageing process	1152
V.	Certain new methods for the investigation of free radicals	1154
VI.	Relation between the changes in the properties of polymers of practical importance and the kinetics of ageing	1155
VII.	Principles of the stabilisation of polymeric materials from the standpoint of the mechanism of ageing	1156
VIII.	A new effective method for the stabilisation of polymers—a "depot" of stabilisers	1157
IX.	The ageing of polymers under special operating conditions	1160
X.	Chemical degradation as a method for the modification of the surfaces of polymers	1163

I. INTRODUCTION

Ten years ago the field of the ageing and stabilisation of polymers was defined as the "chemistry and physics of coupled radical-chain, ionic, and molecular transformations in complex multicomponent systems"[1]. Since then numerous investigations of the detailed mechanism of the ageing processes of polymers and their kinetics as well as studies designed to develop rational stabilisation principles have been carried out[2-6].

Much scope has been found for the application in this field of the theoretical and experimental methods characteristic of chemical physics to the investigation of new phenomena and relations which are of enormous practical importance. A well-founded possibility of formulating the question of ageing and stabilisation of polymers as a multifactor problem, where the study of the changes in the properties of the polymeric material under various conditions can be treated from a single view point, became possible. This field acquired special significance as an important

branch of the chemistry of the solid state with allowance for the specific features of the chemical reactions of macromolecules.

In the course of the development of the first attempts at the identification of the active species responsible for ageing, numerous studies devoted to the elementary steps of the chemical reactions involves these species were carried out and their quantitative kinetic characteristics were determined. New experimental techniques made possible the determination of fine details of the structure of the active centres and at the same time raised the level and importance of the study of the elementary reactions in polymers.

The time is approaching when the ageing process will be treated quantitatively as a set of interrelated elementary reactions no longer in relation to individual model systems but in all cases on the basis of kinetic parameters of elementary processes compiled in tables and handbooks.

The principal task of chemistry, which is to establish relations between the structure of substances and their reactivity, acquires a new significance in the field of the ageing of stabilisation of polymers as the problem of the determination of relations between the changes in the properties of polymers during ageing and the kinetics of the chemical reactions in the polymer.

New principles of the stabilisation of polymers, based on the knowledge of the detailed mechanism of the ageing process, have arisen. New tasks in the field of the ageing and stabilisation of polymers arise in connection with their use in space apparatus and research, in medicine, in the building industry, and in many fields of modern engineering.

The present review deals with certain new results and views referring to the chemical-physical study of the ageing and stabilisation of polymeric materials.

II. THE AGEING OF POLYMERS AS A MULTIFACTOR PROBLEM

The polymeric material in the initial state possesses a definite set of properties y_i which vary with time during ageing, i.e. are functions of time.

The ageing of a polymer consists of a set of its chemical and physical transformations in the course of storage and use. The polymer is then subjected to the action of a wide variety of chemical and physical factors x_i: heat, light, penetrating radiation, oxygen, moisture, corrosive chemical compounds, and mechanical stresses. The operation of these factors creates conditions for the initiation and development of chemical reactions responsible for the ageing of the polymer. For a time the changes in the properties of the polymer may be insignificant from the standpoint of its suitability for practical use (the material is stable). The stability of the material can be characterised quantitatively by its useful life, i.e. the time during which the article or material loses its suitability for practical use under specified influences.

We shall assume that the properties of the material are characterised by a point Y in the space of properties (Fig. 1) at a given instance. The coordinates of this space y_i are quantitative characteristics of the properties, for example, the density, composition, physicomechanical characteristics, dielectric constant, absorption spectrum, etc. The conditions in the practical utilisation of the material can also be characterised by a point in the space of conditions whose coordinates x_i are quantitative characteristics of the conditions: temperature, intensity, and spectral composition of the radiation acting on the polymer, mechanical stress, moisture content, oxygen pressure, etc. The material is suitable for use as long as it possesses the required set of properties, i.e. as long as the point Y does not leave in the course of ageing a certain region of practical suitability ϵ_0 whose dimensions and form may be various depending on the requirements which must be met by the material.

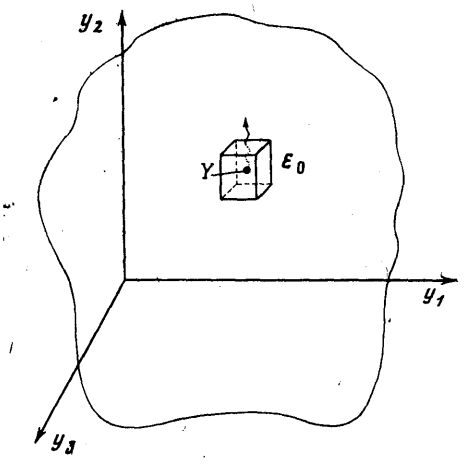


Figure 1. A qualitative picture of the time variation of the set of properties of a polymer y (special case—a point in three-dimensional space). ϵ_0 represents the region of the practical suitability of the polymer.

From the standpoint of chemical physics, the ageing of a polymeric material must be regarded as a process described by a single system of equations suitable for any conditions:

$$Y = f(X, t). \quad (1)$$

The introduction of the characteristics of the conditions into this system of equations makes it possible to determine how the properties of the polymer vary under these conditions. As a result, one can determine the instant when the point Y leaves the limits of any region ϵ_0, i.e. when the material ceases to satisfy the requirements imposed on it.

Thus the useful life of the polymeric materials is determined not only by its physicochemical properties, but also by the conditions under which it is used (X) and the requirements which it must meet whilst being used (ϵ_0).

1. Criteria of the Constancy of the Properties of Polymers

A quantitative treatment of the constancy of the properties of polymers in practice is exceptionally important. Indeed, if it were possible to devise rigorous criteria of the constancy of the properties of polymers, it would be easy to answer the question how far degradation can proceed without the polymer losing its initial properties in practice.

The study of the ageing and stabilisation processes of polymers involves slight chemical transformations in the material which may lead to considerable changes in the physical properties of the specimen.

It is frequently assumed that the properties of a substance virtually do not change if the number of elementary points of damage S (chain rupture, the appearance of new functional groups as a result of chemical reactions) is small compared with the total number of molecules n present in the specimen, i.e. if the condition

$$S/n \ll 1. \tag{2}$$

is fulfilled. If it is assumed that the degree of damage (degradation) δ is defined as the number of breaks per chemical bond in the main chain of the linear polymer molecule, then

$$\delta = \frac{S}{npz}, \tag{3}$$

where $p = M/m$ is the degree of polymerisation (the ratio of the molecular weight of the polymer to the molecular weight of the monomeric unit, which is equal to the number of monomeric units in the macromolecule) and z is the number of bonds in the main chain per monomeric unit. Hence

$$\frac{S}{n} = \delta pz = \delta \frac{M}{m} z, \tag{4}$$

and the condition for the constancy of the properties of the polymer becomes

$$\delta \frac{M}{m} z \ll 1, \text{ or } \delta M \ll \frac{m}{z}. \tag{5}$$

Evidently, for a given type of linear chain, the permissible degree of degradation is smaller the greater the molecular weight.

The use of this criterion leads to the conclusion that polymer materials should have much less constant properties than low-molecular-weight compounds. As an example, we shall compare the capacity for degradation of the polymethylene chains in low-pressure polyethylene ($M = 420\,000$) and in lubricating oil ($M = 420$). In both cases $z = 2$ and $m/z = 14$. We shall assume that 0.01% of all the carbon chains are ruptured in both specimens, i.e. $\delta = 10^{-4}$. We then find $\delta M = 10^{-4} \times 4.2 \times 10^2 = 4.2 \times 10^{-2} \ll 14$ for the lubricating oil, i.e. its properties remain virtually constant. On the other hand, for polyethylene we have

$$\delta M = 10^{-4} \cdot 4.2 \cdot 10^5 = 42 > 14. \tag{6}$$

Hence it follows that the condition for the constancy of the properties is not fulfilled in the latter case.

The significance of the results obtained is that only a small proportion of the molecules were damaged in the lubricating oil, while in the polymer there were several breaks in each macromolecular chain. Indeed $S/n = \delta Mz/m = 10^{-4} \times 420 \times 2/28 \simeq 3 \times 10^{-3}$ for the lubricating oil, while $S/n \simeq 3$ for the polymer.

The simplest criterion of the constancy of the properties of a polymer examined above is by no means universal; it can be used in characterising those properties of the polymer which are determined not only by its chemical structure, but also by the size of its macromolecules. These are, for example, the intrinsic viscosity of the polymer and the light scattering parameters of its dilute solutions. These properties are normally employed for analytical purposes in order to determine the changes in the molecular weight of the polymer during its degradation.

Properties of the polymer of practical importance usually vary with the molecular weight in a complex manner. For example, the stability of the majority of polymers with high degrees of polymerisation usually ceases to depend on the molecular weight, while the glass point, the brittle temperature, and the modulus of elasticity can assume extremum values (Fig. 2). For such a complex dependence of the properties of the polymeric material on its molecular weight, the simplest criterion of their constancy becomes inapplicable. The presence of a region where the properties of the polymer are independent of its molecular weight may result in the properties remaining unchanged for fairly high degrees of degradation. The properties of a polymeric material with a high molecular weight are therefore more stable.

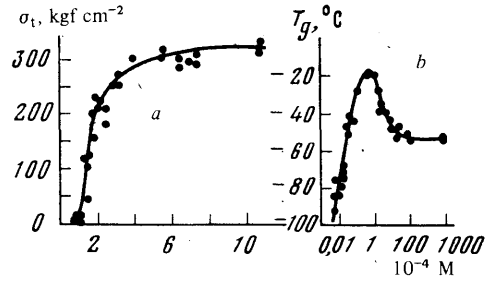


Figure 2. Dependence of the molecular weight M on the tensile strength σ_p of vulcanised natural rubber (a) and on the glass point T_g of poly(ethylene oxide) [7] (b).

It has been established that the reciprocals of many properties of polymeric materials are linearly related to the quantity which is the reciprocal of the molecular weight or the degree of polymerisation [7]:

$$\frac{1}{y} = A\left(1 + \frac{\mu}{M}\right), \tag{7}$$

where y is a characteristic of the properties of the material, for example, breaking strain, while A and μ are parameters. In this case the degree of the change in the property y can be adopted as a criterion of its constancy:

$$\frac{y_0 - y}{y} \ll 1. \tag{8}$$

The degree of damage of the polymer δ is related to its molecular weight by the expression

$$M = \frac{M_0}{1 + \delta M_0}, \tag{9}$$

where M_0 is the molecular weight of the initial polymer. We find from Eqns. (7)–(9)

$$\delta \mu M_0/(M_0 + \mu) \ll 1. \tag{10}$$

Hence the criterion of the constancy of the properties of the material is

$$\delta \ll (M_0 + \mu)/M_0\mu. \tag{11}$$

It follows from Eqn. (11) that for low-molecular-weight compounds ($M_0 \ll \mu$):

$$\delta \ll 1/M_0, \tag{12}$$

i.e. the properties of the substance are less stable the higher its molecular weight. For high molecular weights ($M_0 \gg \mu$), the stability of the material ceases to depend on the molecular weight:

$$\delta \ll 1/\mu. \qquad (13)$$

Unfortunately such criteria, relating the degree of degradation of the polymer to the change in its properties, are also not general. For example, they do not characterise the change in the molecular weight distribution or composition of the polymeric material and do not take into account the change in its molecular structure. In order to determine the extent of the change in the properties of polymeric specimens, one must therefore employ several methods. For example, one may point to methods for the determination of thermal stability from the change in the pressure in the system (manometric method) and from the weight loss (thermogravimetric method), methods based on the study of the change in physicomechanical properties, as well as procedures for the estimation of stability employing data obtained in the study of the polymer degradation products, etc.

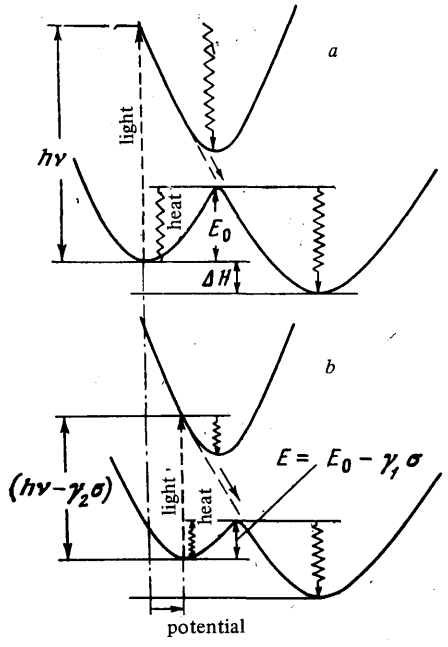


Figure 3. A qualitative picture of the cross-section through the potential surfaces along the elementary chemical reaction coordinate (*a*) and its variation under the influence of mechanical stresses (*b*).

2. The Elementary Step in the Chemical Reaction

In a quantum-mechanical treatment the elementary step of a chemical reaction in a polymeric material, as well as any other system, reduces to the movement of the initial species on the potential energy surface along the reaction coordinate.

Fig. 3 presents a qualitative picture of a section through the potential energy surface for the thermal, photochemical, and mechanical degradation of the polymer. The thermal transition is carried out adiabatically. The phototransition can include a non-adiabatic process stage associated with the absorption of a quantum with the energy $h\nu_0$. When the macromolecule is acted upon by mechanical stresses σ, the minima on the potential curves approach one another, which reduces the values of E and $h\nu$ for which the reaction can take place (in the zeroth approximation the decrease is linear). The rate constant for the elementary step then becomes

$$k = k_0 \exp\left(-\frac{E-\gamma\sigma}{RT}\right), \qquad (14)$$

where γ is a proportionality coefficient, which depends on the form of the potential curves. Since the lifetime of the material, i.e. the time which must elapse before degradation, is

$$\tau_p \propto 1/k,$$

we obtain from Eqn. (14)

$$\tau_p = \tau_0 \exp\left(\frac{E-\gamma\sigma}{RT}\right), \qquad (15)$$

i.e. the familiar Zhurkov equation.

This picture is characteristic of the influence of a field of mechanical forces on any elementary step of the chemical reaction regardless of its nature. When the influence of mechanical stresses on the stability of a polymeric material as a whole or its lifetime is estimated, account must be taken of this influence not on one but on all the elementary steps of the chemical reaction in the ageing process. The linear relationship between the logarithm of the lifetime and the stress

$$\ln\tau_p = \ln\tau_0 + (E-\gamma\sigma)/RT \qquad (16)$$

is therefore an effective characteristic of the process and usually holds over a narrow range of stresses, where the rate of the process is limited virtually by one elementary step. Over a wide range of variation of stresses, this relation is more complex, since the rate-limiting stage of the ageing process can vary with the stress.

3. The Nature of the Active Centres

Molecular reactions are not as a rule important in the mechanism of the ageing of polymers. In practice one must usually take into account reactions involving three types of active species: free radicals, excited species, and to a lesser extent ions.

Free radicals play the main role in the ageing of polymeric materials. This is because reactions involving either the homolytic dissociation of the main chain of the molecule or the homolytic abstraction of atoms or radicals from side groups are characteristic of the majority of polymers.

Ions are formed in polymers usually only in the stage involving the initiation of radiation-induced processes and in processes associated with the degradation of polymers in corrosive media. Data for the formation of ions in the mechanical degradation of polymers on friction and on breakdown of the polymeric material lead to the conclusion that ions play an insignificant role in these processes, their concentrations are low, and they are formed in

secondary reactions associated with the acquisition of electric charge by the polymeric material as the macroparticles move relative to one another. On the other hand, the chemical changes in the material, for example, its mechanical breakdown, are determined by radical and not ionic processes[8].

Electronically excited molecules in the lowest excited singlet (S_1) or lowest triplet (T_0) states play the greatest role in the photochemical ageing of polymers. Two-quantum photochemical processes occurring with participation of the highest triplet states can also be important[9]. The dependence of the quantum yield of a number of photochemical processes on the wavelength of the radiation acting on the polymer indicates the important role of the highest excited singlet states[10].

Together with electronically excited molecules, certain labile species in the excited state can participate in the photochemical ageing process. Thus thermal and photochemical decomposition of certain molecules can lead to the formation of excited ("hot") free radicals[11], which interact more effectively with the medium than the usual ("cold") free radicals. For high intensities of the light during photoageing, free radicals can absorb light quanta and pass to an electronically excited state[12]. The problem of the possible increase of the rate of the chain propagation reaction as a result of the absorption of a light quantum by the free radical is discussed in the literature[13].

The structure and properties of radical active centres involved in the ageing of the polymeric material are various. Table 1 presents typical examples of active centres of this class and demonstrates their role in the ageing process.

EPR has played a particularly important role in the study of radical active centres. It extended enormously the possibilities for the study of the structure of these centres and for the determination of their role in the ageing process.

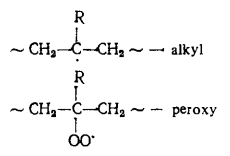
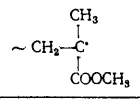
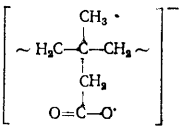
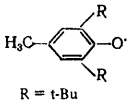
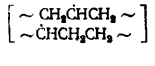
Numerous EPR spectra of the "central" and "terminal" macroradicals of different types are now known (Figs. 4 and 5). The complex structure of the spectrum makes it possible to identify the structure of the macroradical. For example, the spectrum of the central macroradical of polypropylene (Fig. 4) consists of eight components with a splitting of 21 ± 1 G. Hence it follows that in all probability the spectrum refers to the radicals



because here the β-positions relative to the unpaired electron contain seven equivalent protons. Another example is the terminal macroradical of polyformaldehyde whose spectrum consists of a triplet with a splitting of 20 ± 1 G (Fig. 5). Since this type of spectrum corresponds to the interaction of the unpaired electron with two protons, it may be imagined that the given radical has one of two possible structures:



Table 1. Radical active centres and their role in the ageing process.

Type of radical active centre	Example	Formation pathways	Role in ageing process	Influence on direction and rate of ageing process
Central macroradical		chain propagation		
		oxidation of alkyl radicals	chain propagation, cross-linking, and polymer-analogue reactions	change in the structure of side chain, cross-linking, and change in MWD
Terminal macroradical		breaks in macromolecules and depolymerisation	cross-linking and depolymerisation	change in molecular weight and MWD
Low-molecular-weight radical	$\sim \dot{C}H_3$	decomposition of macro-radicals	migration of free valence; лентности	formation of volatile products
Radical-ion		exposure to penetrating radiation and two-quantum photoprocesses	chain initiation	increase of rate of ageing
Inhibitor radicals	 R = t-Bu	reactions involving stabilisers	chain termination and propagation	decrease of rate of ageing
Variable-valence metal ions	Fe^{3+}	catalyst residues, contaminations, and organometallic stabilisers	chain initiation and termination	change in rate of ageing
Radical pairs		decomposition of molecules	destruction in the cage and formation of free radicals	change in rate of ageing

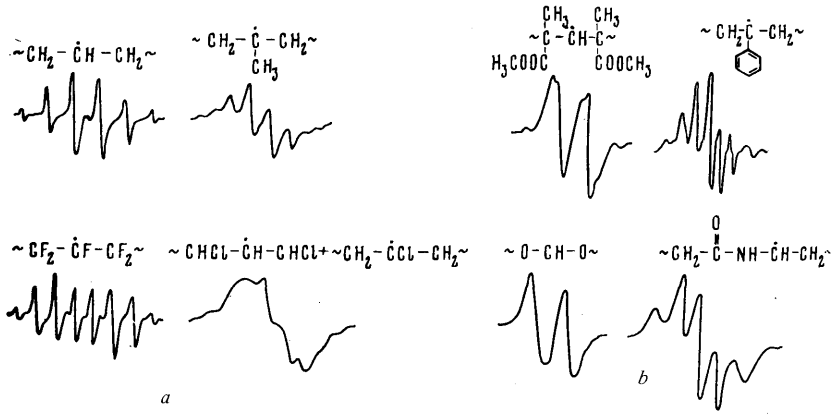


Figure 4. EPR spectra of central macroradicals: *a*) formed under the influence of γ-radiation of polyethylene, polypropylene, Teflon, and poly(vinyl chloride); *b*) formed from poly(methyl methacrylate), polystyrene, polyformaldehyde, and Kapron following the application of mechanical and radiation influences and light.

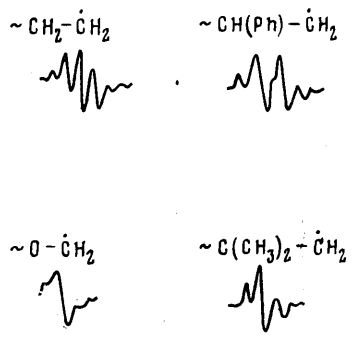


Figure 5. EPR spectra of the terminal macroradicals formed on mechanical degradation and under the influence of radiation for polyethylene, polystyrene, and polyformaldehyde, and polyisobutylene.

A number of workers have devoted particular attention to the interactions of macroradicals with inhibitors and other additives or admixtures present in real polymeric systems. The structures of an enormous number of inhibitor radicals (phenoxy-, nitrogen, and nitroxy-) and their behaviour in the oxidation of the corresponding polymers have been investigated. The scheme presented in Fig. 6 illustrates the conversion of the radicals $R\dot{O}_2$ into the radicals of phenolic inhibitors which occurs in a polypropylene melt at 200°C. Fig. 7 illustrates the EPR spectrum of the inhibitor radical in solid polypropylene [14].

Fig. 8 presents the kinetics of the variation of the concentration of α-naphthol radicals in the oxidation of a polypropylene melt. Evidently during the induction period (curve *2* describes the time variation of Δp_{O_2}) the change in the concentration of inhibitor radicals is autocatalytic. Next a sharp decrease of the amount of In$^{\cdot}$ in the system is observed. The kinetic curve shown agrees satisfactorily with the fact that the inhibitor is consumed as a result of the reaction and the concentration of $R\dot{O}_2$ increases.

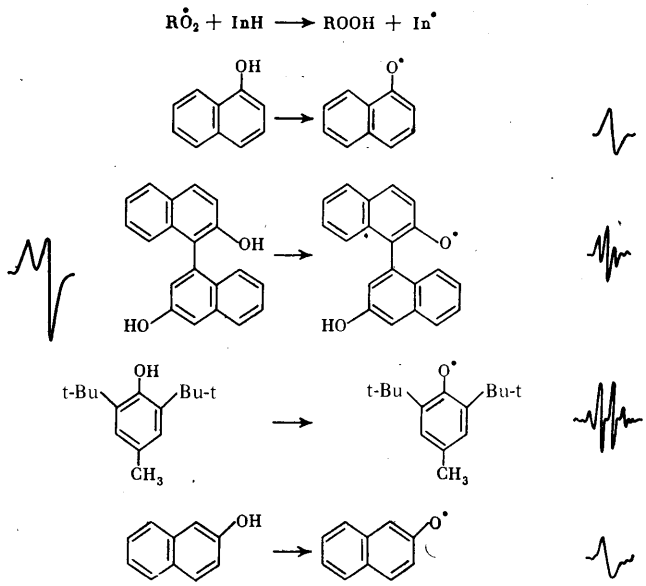


Figure 6. Schematic illustration of the replacement of the radicals $R\dot{O}_2$ by the inhibitor radical (polypropylene, melt); 200°C, p_{O_2} = 400 mmHg.

EPR makes it possible to record a special type of active radical centres—radical pairs. In low-molecular-weight substances EPR permitted the determination of the distance between the unpaired electrons for such stabilised pairs, which usually amounts to 4–7 Å.

Since radical pairs represent in essence the triplet state arising in the interaction of two unpaired electrons, the EPR spectrum reveals the occurrence of two types of transitions between energy levels: with $\Delta M_S = 1$ (transitions in the usual magnetic fields, $g \simeq 2$) and forbidden transitions with $\Delta M_S = 2$ (in "half" fields, $g \simeq 4$) (Fig. 9).

Table 2 presents certain results of the study of the radical pairs in solid polymers at 77 K.

The study of radical pairs in polymers by EPR makes it possible to infer both the nature of the radical components and the mechanism of the elementary step in degradation and structure formation during ageing. For example, analysis of the EPR spectrum for $\Delta M_S = 2$ in γ-irradiated polyethylene led to the conclusion that a pair with the structure

$$\sim CH_2-\dot{C}H-CH_2\sim$$
$$\sim CH_2-\dot{C}H-CH_2\sim$$

is formed and not $\sim\dot{C}H_2\dot{C}H_2\sim$. Evidently such pairs are the kinetic precursors of the cross-links being produced.

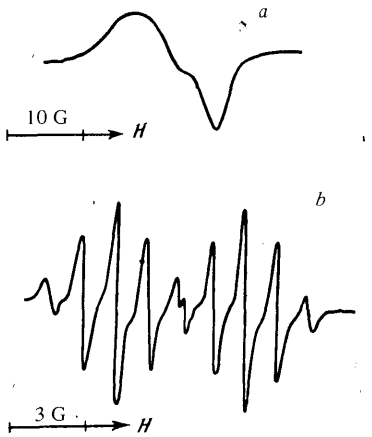
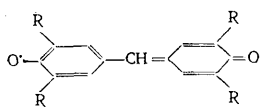


Figure 7. EPR spectrum of the inhibitor radical



(R = t-Bu) in solid polypropylene at 25 °C (*a*) and the spectrum of the same radical in benzene at 25 °C (*b*). In the solid polymer the spectrum is greatly broadened and the hyperfine structure disappears owing to the decrease of the rotation frequencies of the radical [14].

All the foregoing considerations referred to the identification of radical active centres arising in the degradation of polymers. Unfortunately, owing to the lack of special methods, similar to EPR, it is much more difficult to identify active centres in degradation via an ionic mechanism. In this field there have been virtually no systematic studies, with the exception of those which yielded data on the degradation of certain natural polymers in solution.

4. General Characteristics of the Ageing Process

Eqns. (1) are suitable for the description of the ageing process under any conditions. In principle, this problem is susceptible to solution in a general form by modern computer techniques. The thermal degradation, photodegradation, mechanical degradation, oxidation, hydrolytic degradation, etc. processes usually examined are limiting cases of a single ageing process in which the change of the properties of the material is determined by only one factor.

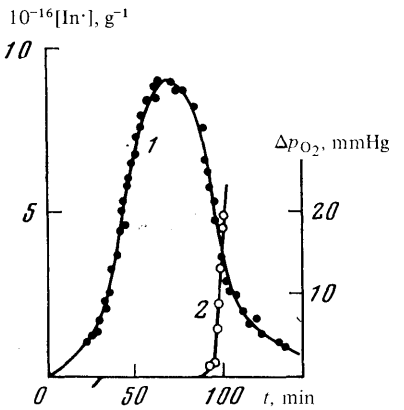


Figure 8. Kinetics of the variation of the concentrations of α-naphthol radicals in the oxidation of fused polypropylene: 1) variation of [In]; 2) kinetics of the absorption of oxygen [15].

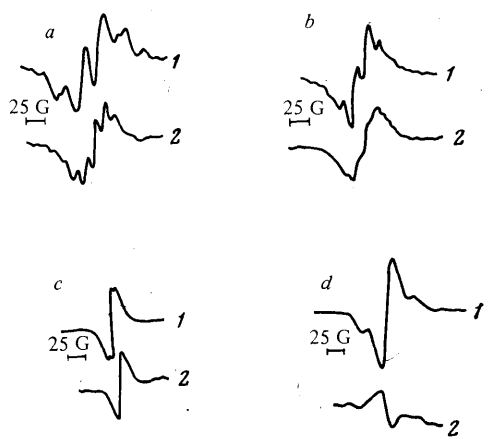


Figure 9. EPR spectra of transitions where $\Delta M_S = 1$ (curve *1*) and $\Delta M_S = 2$ (curve *2*) for polyethylene (*a*), polypropylene (*b*), polyoxymethylene (*c*), and polystyrene (*d*) irradiated with accelerated electrons at 77 K. [16]

In the general case the ageing process includes three main stages (Table 3):

(1) initiation—stage involving the formation of active centres;

(2) the development of ageing—the main stage determining the change in the properties of the polymeric material;

(3) the stage involving the destruction of active centres for ageing.

Table 2. EPR data for radical pairs in solid polymers at 77 K.[16]

Polymer	Ratio of integral intensities $\Delta M_S = 2$ and $\Delta M_S = 1$ in EPR spectra ($\Delta M_S = 2/\Delta M_S = 1 \times 10^5$)	HFS of spectra with $\Delta M_S = 2$
Polyethylene	6.1	16 G
Polypropylene	12.7	15 G
Polyoxymethylene	6.1	unresolved
Poly(ethylene oxide)	1.8	"
Poly(vinyl alcohol)	2.9	"
Cellulose	1.3	"

The physicochemical nature of the initiation stage can be various: in photoageing it is an elementary process with participation of light quanta and molecules in an excited state, while in the radiation-induced process it is a reaction involving ions. In mechanical degradation the initiation stage consists in the dissociation of molecules under the influence of mechanical forces with formation of free radicals.

The development of the ageing process takes place virtually independently of the nature of the initiation. For example, photoageing and radiation-induced ageing proceeds via the same elementary reactions as thermal ageing. External conditions determine in the first place the initiation stage (the formation of free radicals, ions, and excited species). Certain influences affect also the further development of ageing. For example, the presence of oxygen converts any process into an oxidation reaction (thermal degradation becomes thermal oxidation, photolysis becomes photochemical oxidation, and mechanical degradation becomes oxidation in the field of mechanical forces). Temperature influences all the elementary stages with the exception of processes whose activation energy is virtually zero.

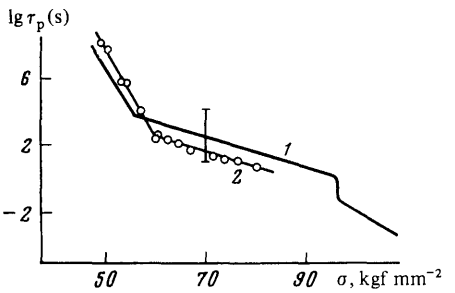
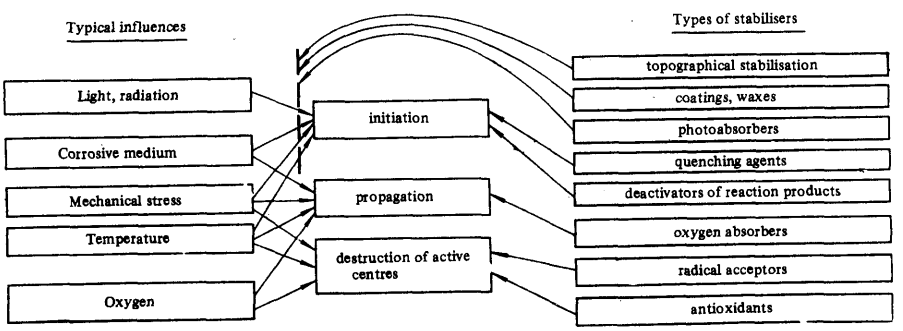


Figure 10. Comparison of the theoretical temperature dependence of the lifetime of polypropylene (calculation based on the radical-chain decomposition mechanism) (curve *1*) with experimental data (curve *2*). The vertical line indicates the error of the calculation.

The complex mechanism of the ageing of polymers makes the relatively simple relations governing a chemical process limited by a single elementary step unsuitable for the description of the ageing process over a wide range variation of conditions. For example, Fig. 10 shows that the semilogarithmic form of the relation between the lifetime of polypropylene and applied stress is not linear as required by Zhurkov's equation. This result has been explained[17] on the basis of a radical-chain mechanism of thermal mechanical degradation including chain initiation stages via the dissociation of the strained bonds of the macromolecules, depolymerisation, chain transfer with formation of a central radical, decomposition of the central radical under the influence of stresses, migration

Table 3. The principal stages in the ageing and stabilisation of a polymeric material.



of the free valence along the central radical, and chain termination:

$$\left.\begin{array}{l} PH \xrightarrow{k_1(\sigma)} 2R^{\cdot}_{term} \\ R^{\cdot}_{term} \xrightarrow{k_2} R^{\cdot}_{term} + M \\ R^{\cdot}_{term} + PH \xrightarrow{k_3} PH + R^{\cdot}_{cent} \\ R^{\cdot}_{cent} \xrightarrow{k_4(\sigma)} R^{\cdot}_{term} + PH \\ R^{\cdot}_{cent} \xrightarrow{k_5(\sigma)} R^{\cdot}_{term} \\ 2R^{\cdot}_{term} \xrightarrow{k_6} PH \end{array}\right\}. \qquad (17)$$

where M is the monomer and PH the polymer. Account was taken of the influence of the applied stress, in accordance with Zhurkov's equation, on the elementary steps in the decomposition of the polymer (k_1) and the macroradical (k_4 and k_5).

For small stresses, Eqn.(15) should hold; under these conditions, τ_0 and F are effective quantities and do not refer to any one elementary stage of the process:

$$\tau_p = a\sqrt{\frac{k_6}{k_1 k_3^2}}\exp\left(\frac{-\gamma\sigma}{RT}\right), \qquad (18)$$

where a is a proportionality coefficient which depends on temperature. Accordingly, the pre-exponential factor for this process is not the average period of the thermal vibrations of the atoms, as in Eqn.(15), but is determined by the ratio of the pre-exponential factors associated with the rate constants for the elementary thermal degradation reactions.

Over a wide range of stresses, Eqn.(18) ceases to hold, because for large stresses the degradation process is so fast that there is insufficient time for the establishment of a quasi-stationary concentration of radicals. Calculation shows that, under these conditions, the plot of the logarithm of the lifetime against stress should be curved. This type of relation has been observed experimentally in the study of the thermal mechanical degradation of polypropylene[17].

Fig. 10 compares the experimental data with the results of a computer calculation using the known rate constants for the elementary reactions in the kinetic scheme (17). Not only a qualitative but also a quantitative agreement between calculation and experiment is evident; the break in both relations corresponds to approximately the same applied stresses.

The hypothesis of a radical-chain mechanism of thermal mechanical degradation suggests that inhibitors of free radical reactions, which increase the stability of the polymer on thermal degradation, should also increase its lifetime on application of a mechanical load. Indeed, when a stable nitroxy-radical, which functions as an acceptor of alkyl radicals, is introduced, the lifetime of nitrocellulose increases significantly (Fig. 11*a*).[18] On the other hand, an increase of the rate of initiation of the ageing process should decrease the lifetime of the polymers. An appreciable decrease of the lifetime of stressed polycarbonate, in which an additional amount of free radicals was produced as a result of the thermal decomposition of the benzoyl peroxide introduced into the polymer or via the photolysis of added iron(III) chloride, has been observed[79] (Fig. 11*b*).

For low stresses, the main source of radicals is the decomposition of initiators; the lifetime of the polymer in their presence decreases greatly and depends only slightly on the applied stress. For large stresses, free radicals are generated mainly as a result of the mechanical degradation of macromolecules, so that the lifetime of the polymer hardly changes after the introduction of additives.

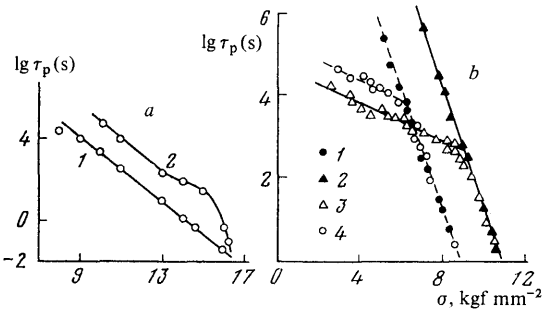


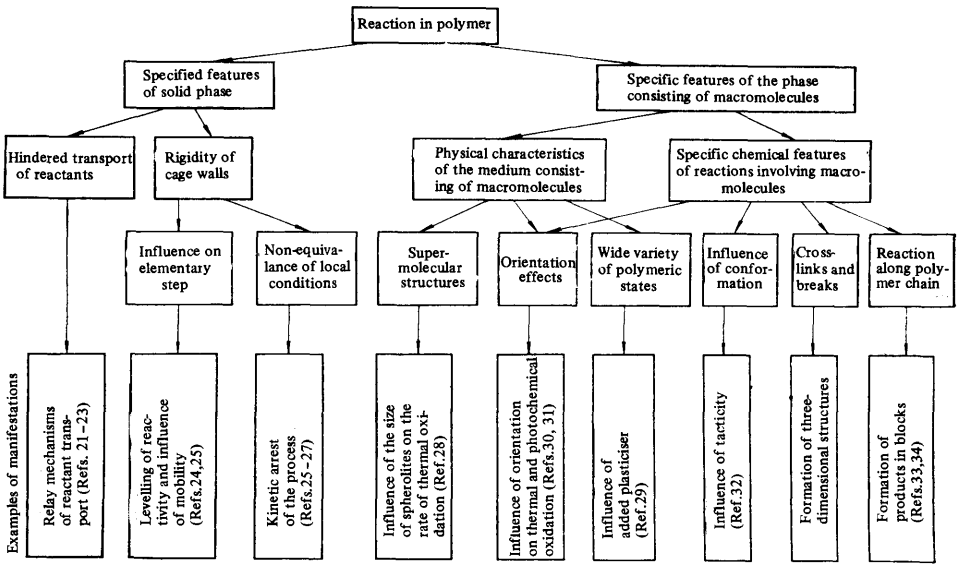
Figure 11. Variation of the lifetime of the polymer as a result of the introduction of inhibitors (*a*) and initiators (*b*) of radical reactions: *a*) nitrocellulose [1) pure; 2) with added 0.3% of 4-ethyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical]; *b*) polycarbonate [1) and 2) pure; 3) with added 0.34% $FeCl_3$ under the influence of the light from a mercury lamp; 4) with added 0.5% of phenyl peroxide; 2) and 3) 20°C; 1) and 4) 70°C].

The internal stresses arising the specimen, for example, during its hardening, can also alter the rate of ageing of the polymer. For example, cross-linked polyester-urethanes, obtained at 30°C, decomposes with an activation energy $E = 21-23$ kcal mole^{-1}, while the specimens synthesised at 60°C decompose much more slowly with $E = 46-50$ kcal mole^{-1}. It has been shown that this difference is associated with the competition between the urethane formation reaction and the relaxation of the internal stresses in the specimen as a result of conformational transitions[20]. At low temperatures there is insufficient time for the occurrence of the conformational transitions during synthesis, so that a polymer with strained bonds is formed, which facilitates its thermal degradation. At elevated temperatures there is sufficient time for relaxation processes during the synthesis of cross-linked polyurethanes, the number of strained bonds formed is very small, and the resulting polymer has a higher thermal stability.

III. CHARACTERISTICS OF THE CHEMICAL REACTIONS IN THE POLYMER MATRIX

As a subdivision of the chemistry of the solid state, the field of the ageing and stabilisation of polymers deals with the study of complex coupled radical-chain, ionic, and molecular reactions under the conditions of polymer matrices involving in the chemical process the very polymer molecules forming the matrix. Table 4 illustrates the principal features of the chemical reactions in the polymer matrix (PM). They have distinctive features as both solid-phase reactions and reactions of high-molecular-weight compounds.

Table 4. Characteristics of the chemical reaction in the polymer matrix.



As in any solid-phase process, the kinetics of the reactions in the polymer matrix are influenced significantly by the transport of reactants and the stability of the cell walls surrounding the reactive centres. The first factor is particularly important in cases where the reactive centre is localised on a macromolecule. The diffusion of such centres is hindered and complex models, including many macromolecules or intermediate labile centres—the so-called models of the relay migration of the active centre—have been considered to explain processes with participation of such centres[21-23].

The stability of the cage environment of the active centre leads to two qualitatively different effects. On the one hand, the contact time between the reactants which have entered a single cage is much greater than in the liquid phase, which can reduce many types of steric hindrance and can lead to an appreciable degree of levelling of the reactivities of the species in the solid phase compared with the liquid phase[24,25]. On the other hand, the polymeric material usually contains defects, many of the formations in which can exist for a fairly long time. As a result of the wide variety of these defects, the occurrence of elementary chemical reactions under kinetically non-equivalent conditions is typical for a polymer matrix. This is manifested by the kinetic arrest of certain chemical reactions under conditions where the reactants have still not been exhausted[25,26] and also by the obligatory occurrence of certain photochemical processes which cannot be inhibited despite the virtually complete quenching of the luminescence of the excited species propagating the process[27].

The polymer matrix cannot be regarded as a normal solid matrix. The polymeric material has as a rule a complex structure, because it is possible to distinguish in it a number of regions differing in the degree of order in the arrangement of the polymer chains and hence in the chemical reactivity. The most ordered regions, with a structure close to that of an ideal crystal, are characterised by the minimum free energy and close packing of the polymer chains and have a comparatively low reactivity. Crystalline regions with different structural defects, for example, dislocations, can exhibit a greater permeability with respect to small molecules and a somewhat higher reactivity. Finally, the least ordered amorphous regions are characterised by a low chain packing density, an increased concentration of impurities, and the maximum reactivity.

Because of this, the ageing of a polymeric material is influenced by its supermolecular structure[28]. Small amounts of added plasticiser alter the structure of the polymer matrix and change sharply the rate constant for the processes occurring in it[29]. Orientation effects, which result in a change of the physicomechanical properties of the polymeric material and of the rate and direction of the chemical reaction, are characteristic of the polymer matrix[30,31]. In the course of the ageing of the polymeric material, degradation processes and cross-linking reactions of the macromolecules, which are characteristic of high-molecular-weight compounds only and which lead to a change of the molecular weight distribution and sometimes to the formation of cross-linked three-dimensional structures, take place in the polymeric material in the course of its ageing.

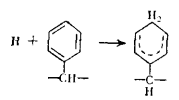
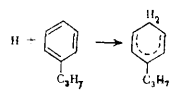
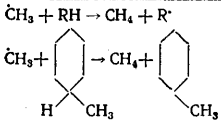
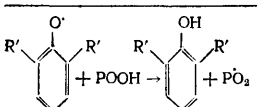
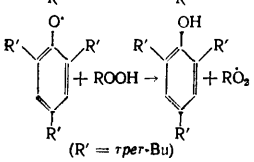
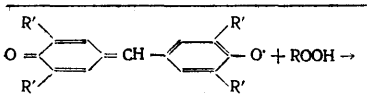
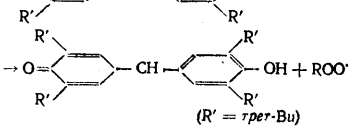
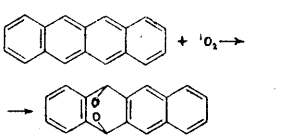
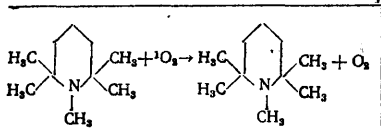
The kinetics of reactions in which high-molecular-weight compounds participate are influenced also by the conformations of the latter[32]. Furthermore, there are data indicating the development of the reaction along the polymer chain, which leads to the formation of reaction products in blocks, in the form of long sequences along the macromolecular chain[33,34].

1. The Influence of the Molecular Mobility of the Polymer Matrix on the Rate Constants for the Elementary Reactions Occurring in It

The dynamics of the molecular movements of the polymer exerts a significant influence on the kinetics of chemical reactions. This is caused by the change in the translational diffusion coefficients of the low-molecular-weight

reactants and the frequencies and amplitudes of segmental movements of the macromolecules and macroradicals, resulting in a change of the frequency of encounters of the reacting species. Furthermore, the molecular mobility of the medium influences directly the elementary step of the chemical reaction.

Table 5. The rate constants for chemical reactions in solid polymers and in the liquid phase.

Reaction	Polymer or solvent	t, °C	k, litre mole^{-1} s^{-1}	Refs.
	polystyrene	25	$1\cdot10^{4}$	35
	n-heptane	23	$3.3\cdot10^{8}$	36
$\dot{C}H_3 + RH \rightarrow CH_4 + R^{\cdot}$	polypropylene	100	0.2	37
	n-heptane	100	$3.8\cdot10^{3}$	36
	polypropylene	25	$4.5\cdot10^{-3}$	38
 (R′ = *tper*-Bu)	benzene	25	0.11	39
	polypropylene	25	$3.0\cdot10^{-5}$	14
 (R′ = *tper*-Bu)	benzene	25	$5.6\cdot10^{-4}$	
	polystyrene	20	$2.0\cdot10^{5}$	40
	methylene chloride	20	$1.8\cdot10^{7}$	
	polystyrene	20	$1.0\cdot10^{6}$	41
	methylene chloride	20	$5.4\cdot10^{7}$	

The rate constants for a number of bimolecular reactions in solid polymers are significantly lower than in the liquid phase. Certain examples of this kind are listed in Table 5. The decrease of the rate constants on passing to solid polymers is not associated solely with diffusion-dependent obstacles. The rate constants for the encounters between the reactants, estimated from the diffusion coefficients of the low-molecular-weight substances, exceed by several orders of magnitude the experimental rate constants for the reactions, i.e. these reactions are not diffusion-controlled.

The molecular mobility of the medium is known to influence the kinetics of the destruction of macroradicals in solid polymers which entails a decrease of the rate of destruction on passing from the amorphous to the crystalline phase [41-43], a decrease of the rate constant for destruction in oriented specimens compared with non-oriented specimens [44,45], an increase of the stability of the macroradicals on cross-linking of the polymer [46,47], an increase of the rate of destruction of macroradicals in three-dimensional polymers with the increase of the length of the oligomeric block [48], etc.

Molecular mobility can be varied in a controlled manner by changing the external pressure and by introducing chemically inert solvents into the polymer (plasticisation).

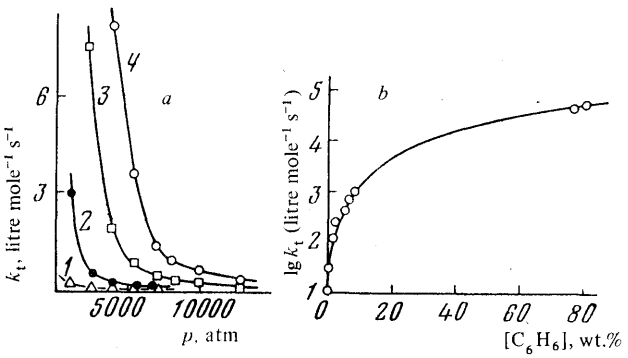


Figure 12. The influence of pressure (*a*) and plasticisation (*b*) on the rate constants for the destruction of free radicals in the polymer: *a*) poly(methyl metacrylate) [temperature (°C): 1) 80; 2) 100; 3) 120; 4) 130]; *b*) polystyrene with benzene as plasticising agent; $T = -10$°C.

In amorphous polymers at temperatures above T_g the radical recombination rate constants k_t decrease with increasing pressure p (Fig. 12*a*) [49-52]. At temperatures below T_g the influence of pressure on k_t is comparatively small. The strongest effect is observed for low values of p; at a pressure higher than a critical value p_{cr} the constant k_t depends only slightly on p. For $p < p_{cr}$, the dependence of k_t on p is described by the relation [53]:

$$k_t = k_t^0 \exp\left(-\frac{E + pV^*}{RT}\right), \qquad (19)$$

where V^* is the activation volume; here E sometimes changes to p. Pressure apparently influences the kinetics of the destruction of the macroradicals by altering the molecular mobility of the medium. With increase of

pressure, there is an increase of the density of the polymer and a decrease of the intensity of molecular movements, which is manifested, for example, by an increase of T_g, a decrease of the free volume and the melting point of the polymer, etc.

Eqn. (19) shows that an increase of p affects k_t in the same way as a decrease of temperature. The glass point is apparently attained at $p = p_{cr}$.

The plasticisation of the polymers has a significant influence on the kinetics of the destruction of macroradicals. The destruction of peroxy-radicals in polystyrene[23] (Fig. 12*b*) and polypropylene[54,55] is accelerated by small amounts of added chemically inert solvents. The accelerating effect can be explained only by the increase of molecular mobility in the polymer.

According to Roginskii and Miller[55], the variation of k_6 in solid polypropylene in the presence of *o*-dichlorobenzene is correlated with the frequency of the rotation of the paramagnetic probe characterising the mobility. Plasticisation of the polymer also leads to an increase of the liberation of radicals from the cage on decomposition of the initiator[14,55,56] and to an increase of the rate of chain oxidation of polypropylene[55].

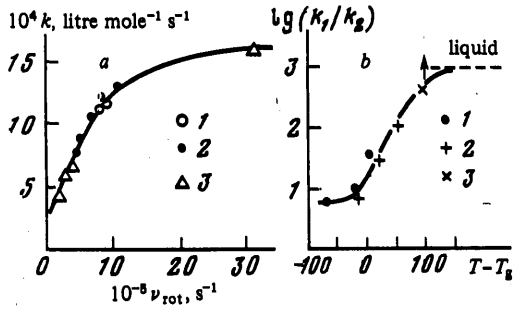


Figure 13. Relation between the rate constants for chemical reactions and the molecular mobility of the medium: *a*) rate constant for the reaction of 4-benzyloxy-2,2,6,6-tetramethylpiperidinyloxy-radical with 4,6-di-t-butyl phenol in various polymeric matrices plasticised with benzene (60°C) [1) polyethylene; 2) polypropylene; 3) polystyrene]; *b*) the ratio of the rate constants for the quenching of singlet oxygen by nickel dibutyldithiocarbamate and nickel ortho-ethoxy-(3,5-di-t-butyl-4-hydroxybenzyl)phosphonate [*O*-ethyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate?] at different temperatures in different polymer matrices: 1) polystyrene; 2) BMK-5 copolymer; 3) polybutadiene.

The influence of molecular mobility on the reactions of phenoxy-radicals with the hydroperoxides of polyolefins[14,38] and of nitroxy-radicals with phenols in solid polyolefins has also been considered. The rates of these reactions are independent of the nature of the polymer and increase following the addition of aromatic solvents, whose role reduces to an increase of molecular mobility. Here the increase of the rate constant is correlated with the increase of the frequency of rotation of the paramagnetic probe[38,57] (Fig. 13*a*). Another phenomenon characteristic of the solid polymer matrix, the levelling of reactivity compared with the liquid phase for a series of compounds undergoing the same reaction, is also associated with the decrease of the molecular mobility of the medium in the polymer matrix.

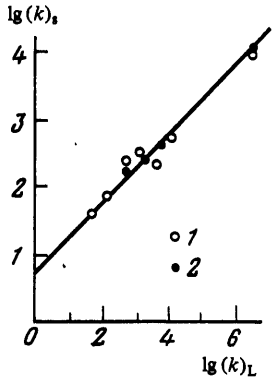


Figure 14. Logarithmic form of the dependence of the efficiency of the quenching of singlet oxygen by a number of quenching agents at different classes in polystyrene (1) and the butyl methacrylate–methacrylic acid copolymer (2) on the efficiency of the quenching by the same agents in liquid solution.

The levelling phenomenon was first observed for the reaction of a number of antioxidants with free radicals in solid polymers[24]. An analogous effect has been observed in processes with participation of singlet oxygen $^1O_2$.[40] Fig. 14 illustrates the logarithmic form of the relation between the efficiency of the quenching of $^1O_2$ by a number of quenching agents of different chemical types in a solid polymer on the efficiency of the same compounds in a liquid solution for two different polymer matrices (polystyrene and the butyl methacrylate–methacrylic acid copolymer). Evidently the range of differences between the efficiencies for the given series of quenching agents is over five orders of magnitude in the liquid phase and less than three orders of magnitude in the solid phase.

The relation between the observed phenomenon and the molecular mobility of the medium is demonstrated in Fig. 13*b*.[58] The degree of levelling presented in the figure is defined as the ratio of the quenching constants for two quenching agents with different efficiencies. The difference between the experimental temperature and the glass point of the matrix is a measure of the molecular mobility of the medium. Evidently the data obtained for different polymer matrices fit the same relation despite the fact that their absolute glass points differ by hundreds of degrees. The levelling of reactivity is apparently determined solely by the mobility of the medium and is independent of the chemical nature of the polymer.

The levelling phenomenon can be explained quantitatively by a change in the nature of the movement of a pair of reacting species in the solid matrix compared with the liquid phase[59]. It has been found that, for isotypical reactions, whose rate is limited by steric hindrance, the relative reactivities of the species in the solid polymer

(k_S) and in the liquid phase (k_L) are linked by the relation

$$\frac{(k_1)_S}{(k_2)_S} = \sqrt{\frac{(k_1)_L}{(k_2)_L}}. \quad (20)$$

Eqn. (20) is of considerable practical importance, since it is possible to select with its aid various stabilisers for polymeric materials (antioxidants and quenching agents) on the basis of much less laborious experiments, carried out in model liquid-phase systems.

2. The Influence of the Molecular Mobility of the Medium on the Kinetics of Reactions in Polymers

The equivalence of the local properties of the environment of the reactive centres and hence the sterically different activities of these centres is characteristic of polymers as structurally inhomogeneous systems. Chemical reactions occur in the first place in those regions where the conditions are most favourable. As a result, the concentration of active centres in these regions diminishes and there is a corresponding decrease of the effective rate constant for the reaction averaged with respect to the entire specimen. Different kinds of relaxation processes, which alter the local conditions around the reactive centres causing the migration of these centres to regions favouring chemical reaction, act in the opposite direction.

We shall introduce the concept of characteristic times of processes occurring in the polymer matrix. The chemical reaction time τ_{chem} can be characterised by a quantity which is the reciprocal of the rate of change of the relative concentration of the reactants (c/c_0):

$$\tau_{chem} = \left(\frac{d(c/c_0)}{dt}\right)^{-1}. \quad (21)$$

The duration of relaxation processes τ_c, which restore the equilibrium distribution of the local properties around the reaction centres disturbed by the chemical process, can be characterised by the correlation time of the reacting species with respect to all local properties of the medium which determine the reactivity of these species. If

$$\tau_{chem} \gg \tau_c, \quad (22)$$

the relaxation processes are so fast that the chemical reaction virtually does not alter the equilibrium distribution of the reactants and any reacting species has average properties throughout the entire process. Consequently the process as a whole will be described by a single average rate constant, as in classical liquid- or gas-phase kinetics. If condition (22) is not fulfilled, the reacting species will exist under non-equivalent conditions during the chemical process and the effective rate constant for the chemical reaction will gradually decrease.

The rate of change of the macroscopic concentration of the reacting substances is described by an integrodifferential equation which assumes the following form for the simplest unimolecular reaction:

$$\frac{d[A]}{dt} = -\int k(u) A(u) du, \quad (23)$$

where $k(u)$ is the rate constant for the chemical reaction and the local conditions characterised by the parameter u; the form of the function $k(u)$ is independent of time, since it determines the relation between the probability of the chemical reaction and the local properties of the medium; $A(u)$, the density of the distribution of the concentration of substance A with respect to the parameter u, varies in time owing to both the chemical reaction of substance A, described by Eqn. (23), and the relaxation and diffusion processes which alter the local properties of the medium around the reaction centre.

Eqn. (23) is converted into the classical expression when the local properties of the medium do not influence the probability of the chemical reaction:

$$k(u) = K^0 = \text{const} \quad (24)$$

or if the function $A(u)$ can be represented by the product of the concentration of substance A and the time-invariant characteristic form of the distribution of the local properties of the medium $\rho(u)$, i.e. if

$$A(u) = [A]\,\rho(u). \quad (25)$$

In such cases the rate of decrease of the macroscopic concentration of substance A is described, as in the liquid or gas phase, by the exponential relation

$$[A] = [A]_0 e^{-k_0 t} \quad (26)$$

or

$$[A] = [A]_0 e^{-\int k(u)\rho(u)du \cdot t}.$$

In all remaining cases the process inhibition is greater.

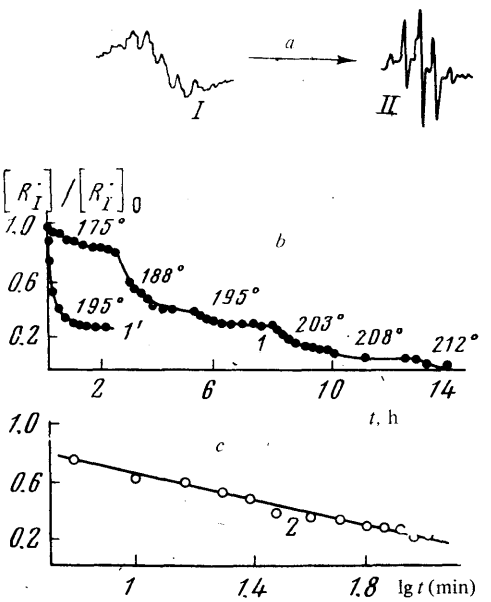


Figure 15. *a*) EPR spectrum of polymethacrylic acid (PMAA) macroradicals with the free valence localised at a tertiary carbon atom of the main chain (I) and of the terminal macroradicals (II) formed as a result of the thermal decomposition of the radicals (I); *b*) kinetic curves (curves *1* and *1'*) for the thermal decomposition of radicals (I) in PMAA in the temperature range 175–212 K; 2) a modification of the kinetic curve *1'* obtained by plotting $[\dot{R}_I]/[R_I]_0$ against lg*t* at 195 K.

Such inhibition is fairly common in chemical processes occurring in polymer matrices at temperatures below the glass point under conditions such that the molecular mobility of the medium is low. For a comparatively low degree of conversion, the reaction is inhibited but does not come to a complete stop. The inverse semilogarithmic $A/A_0 - \lg t$ form of the kinetic curve for the variation of the concentrations of the reactants is usually a straight line up to high degrees of conversion of the substance (Fig. 15)[66].

The phenomenon of such kinetic arrest of the reaction has now been observed in many processes in solid polymers: the destruction of the radicals involved in radical pairs[60], the oxidation of radicals[61], postpolymerisation[62], inhibited oxidation[63], oxidation by singlet oxygen[64], thermal isomerisation and photoisomerisation[65], decomposition of macroradicals with chain rupture[66], and dark cyclisation of spiropyrans[67]. These results can usually be described on the basis of the idea that, throughout the process, the reacting species are as it were frozen under different, but constant during the entire process, local conditions, i.e. $\tau_{chem} \ll \tau_C$. The equations of classical kinetics are then applicable only to species under identical conditions, i.e. for a distribution density $A(u)$. The inverse semilogarithmic plot is linear if it is assumed that the initial distribution $A(u)$ with respect to the free energy of activation for the process $\Delta G = E_a + IS$ is rectangular:

$$(A(u))_{t=0} = 1/S_0 \text{ when } 0 < u < S_0;$$
$$(A(u))_{t=0} = 0 \quad \text{when} \quad 0 > u > S_0. \qquad (27)$$

The solution of Eqn. (23) can then be written as follows:

$$[A] = -\frac{[A]_0}{S}\left[\ln(1.76k_0) - S_0 + \ln t - \frac{E_a}{RT}\right]. \qquad (28)$$

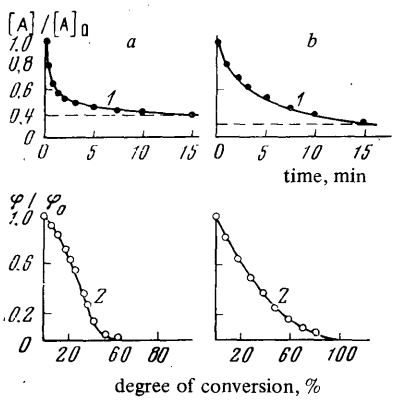


Figure 16. The photochemical reaction (λ = 365 nm) of anthracene in poly(methyl methacrylate): *a*) vacuum; *b*) air; 1) process kinetics; 2) dependence of the quantum yield on the degree of conversion of anthracene.

It has been shown that the semilogarithmic plot should remain linear for a rectangular distribution and for any law governing the consumption of A for reaction orders between first and third[68]. The change in the order of the reaction involving the consumption of A alters only the coefficient of the pre-exponential factor k_0 in Eqn. (28).

A characteristic feature of the kinetics of reactions in a solid polymer, the "stepwise" kinetics involving a kinetic arrest, can be used to regulate the corresponding processes. By changing the conditions, the temperature, and the viscosity, it is possible to accelerate greatly the inhibited process. On the other hand, without allowing the conditions to be altered, it is possible to avoid undesirable ageing reactions.

The decrease of the effective rate constant for the chemical reaction in the polymer matrix gives rise to the possibility of the "kinetic stabilisation" of substances fulfilling various functions in the polymeric material. For this purpose, one introduces into the polymer the substance at a concentration greater than necessary and the part of the substance under conditions favourable for chemical reaction is decomposed. The remaining additive is preserved by virtue of the kinetic arrest of reactions in polymers.

Anisimov[69] introduced anthracene into poly(methyl methacrylate) (PMMA) and illuminated the specimen with light at λ = 365 nm. Part of the anthracene was consumed as a result of the photochemical reaction; the remainder was as it were stabilised in the polymer (Fig. 16).

Hydrocarbons with condensed rings, of which anthracene is a representative, are widely used as luminescent labels for the recording of information, i.e. as photochromic materials. The kinetic stabilisation of these compounds in a polymer matrix is therefore of practical importance.

IV. QUANTITATIVE CHARACTERISTICS OF THE ELEMENTARY STAGES OF THE AGEING PROCESS

During recent years, apart from the study of the kinetics of the overall ageing process, numerous measurements have been made of the rate constants for the individual elementary stages of the complex process. The methods of their measurement in solid polymers do not differ in principle from those used in the liquid phase. The data obtained refer mainly to the thermal oxidation of polymers.

The rate of initiation w_i was measured with the aid of different versions of the method of inhibitors[63,70,71], based on the determination of the rate of consumption of a radical acceptor (X) taken at a concentration sufficient to cause the termination of all the oxidation chains. The independence of the rate of consumption of the acceptor of its concentration is an experimental criterion of the fulfilment of this condition:

$$w_i = n\frac{d[X]}{dt},$$

where n is the number of chains terminated by one acceptor molecule. Phenolic and amine inhibitors as well as stable radicals, mainly nitroxy-radicals, have been used as acceptors.

A method based on the determination of the induction period of the inhibited oxidation is also employed[72]. Some of the rate constants for the initiation of the reactions in solid polymeric media are listed in Table 6.

The parameters $k_p/\sqrt{k_t}$, which is the ratio of the rate constants for the chain propagation reaction (k_p) and the square root of the rate constant for the chain termination reaction (k_t) and characterises the oxidisability of the

polymer, is determined from the rate of the chain initiation of the oxidation process (w_i = const.); one can use as initiators not only specially added low-molecular-weight substances but also a "natural initiator"—a polymer hydroperoxide [10].

Table 6. The rate constants for initiation (k_i) in the decomposition of radical initiators in solid polymers.

Initiator*	Polymer	k_i, s^{-1}	References
AIBN	polypropylene	$5.1\cdot10^{17}$ exp (—37 000/*RT*)	70
AIBN	polystyrene	$8.4\cdot10^{13}$ exp (—30 800/*RT*)	63
CPC	polystyrene	$4.6\cdot10^{14}$ exp (—29 600/*RT*)	63
Benzoyl peroxide	polybut-1-ene	$1.5\cdot10^{-6}$ (80° C)	73
Cumenyl peroxide	polyethylene	$1.4\cdot10^{-6}$ (115° C)	74
Butyryl peroxide	polystyrene	$1.3\cdot10^{-7}$ (80° C)	75
Polymeric hydroperoxide	polypropylene	$1.0\cdot10^{13}$ exp (—30 500/*RT*)	70
Polymeric hydroperoxide	polyethylene	$1.6\cdot10^{14}$ exp (—35 000/*RT*)	76
2-t-Butylperoxy-2,4,6-tri-t-butylcyclohexa-3,5-dienone	polyprolyene	$4.5\cdot10^{16}$ exp (—35 500/*RT*)	77

*Notation: AIBN = azobisisobutyronitrile; CPC = cyclohexyl peroxydicarbonate.

Table 7. The chain propagation (k_p) and termination (k_t) rate constants in the oxidation of solid polymers.

Polymer	*t*, °C	$k_p/\sqrt{k_t}$, $kg^{1/2}\ mole^{-1/2}\ s^{-1/2}$	k_t, kg mole^{-1} s^{-1}	k_p, kg mole^{-1} s^{-1}
Polypropylene (atactic)	80	$1.8\cdot10^{-3}$ [79]	$1.2\cdot10^{3}$ [79]	0.055 [79]
Polypropylene (isotactic)	80	$8.1\cdot10^{-4}$ [70]	$3.5\cdot10^{3}$ [55]	0.1 [70]
Polyethylene	80	$4\cdot10^{-5}$ [60]	$4.8\cdot10^{4}$ [81]	$7.7\cdot10^{-3}$ *
Polybut-1-ene	80	$6.5\cdot10^{-4}$ [73]	—	—
Poly-4-methylpent-1-ene	80	$4\cdot10^{-4}$ [73]	—	—
Polystyrene	20	—	7.7 [61]	$0.7\div3\cdot10^{-4}$ ** [61]
Poly(methyl methacrylate)	20	—	0.5 [22]	$8\cdot10^{-4}\div8\cdot10^{-6}$ ** [69]

*Calculated from the data of Shilov and Denisov [80] and Davis et al. [81].
**Values obtained from data for the "stepwise" kinetics of the transformation $R\dot{O}_2 \rightarrow \dot{R}$ in an inert atmosphere.

The rate of absorption of oxygen W is related as follows to w_i and $k_p/\sqrt{k_t}$:

$$W = (k_p/\sqrt{k_t})\,[RH]\,\sqrt{w_i} + mw_i,$$

where m is the number of oxygen molecules absorbed in the oxidation chain initiation and termination steps.

The absolute rate constant for chain termination is determined either from the absolute concentration of peroxy-radicals in the initiated process [78,79]

$$k_t = \frac{w_i}{[\dot{RO}_2]^2},$$

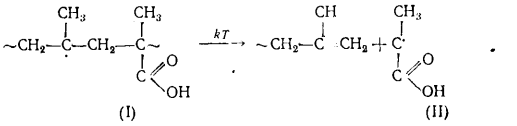
or by fitting an expression to the rate of destruction of radicals after brief exposure to light [54]:

$$\frac{[\dot{RO}_2]_0}{[\dot{RO}_2]} = 1 + k_t\,[\dot{RO}_2]_0\,t.$$

The latter method does not require a preliminary determination of w_i and the kinetic law governing the destruction of the radicals is established directly in the experiment. Table 7 lists the rate constants and the kinetic parameters $k_p/\sqrt{k_t}$ determined by these methods.

Together with the determination of the rate constants for the main stages of the chain thermal oxidation process, the detailed mechanism of the reactions of many macroradicals propagating the ageing process has now been investigated. It has been shown by EPR that the macroradicals of poly(methacrylic acid), generated at 77 K and having the free valence located at a tertiary carbon atom of the main chain as in (I) (Fig. 15*a*), are converted, on raising the temperature, into terminal radicals stable at room temperature, which are formed on thermal decomposition of (I).

The rate constants for the decomposition of the macroradicals of poly(methacrylic acid) with rupture of the main macromolecular chain were measured for the first time by Davydov et al. [66]:



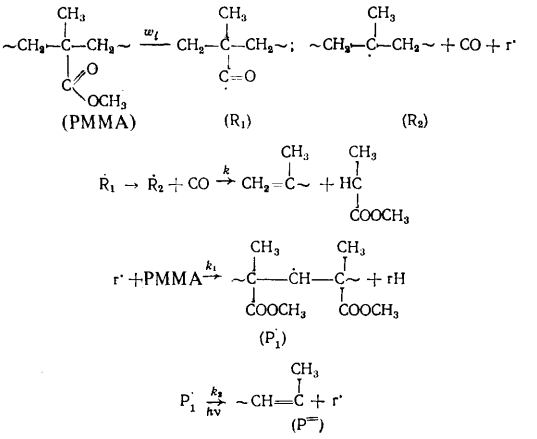
(I) (II)

Above 212 K, this process is described by a first order equation with rate constants defined by expressions of the type

$$k = 10^{13\pm1}e^{-16500/RT}\ (s^{-1}).$$

On the other hand, at lower temperatures the molecular mobility in poly(methacrylic acid) decreases and, on converting radicals (I) into radicals (II), the reaction undergoes a kinetic arrest (Fig. 15), which can be interpreted qualitatively on the assumption of a rectangular distribution of the rate constants for the decomposition of radicals (I) with respect to activation energies, which has the parameters E_{min} = 13 kcal mole^{-1}, E_{max} = 16.1 kcal mole^{-1}, and $\lg k_0\,(s^{-1}) = 13.7$.

The free radical mechanism of the photolysis and thermally initiated and photoinitiated conversion of PMMA has been investigated at temperatures below 50 °C [82–85] where depolymerisation virtually does not occur. Six macroradicals were identified and the mechanism of their thermal reaction and photoreaction was investigated:



(PMMA) (R_1) (R_2)

(P_1)

($P^{=}$)

$$r^{\cdot} + P^{=} \rightarrow \sim\overset{\overset{H}{|}}{C}-\overset{\overset{r}{|}}{C}-CH_3 \quad (P_2^{\cdot})$$

$$P_2^{\cdot} + P^{=} \xrightarrow{k_4} P_{2(1)}^{\cdot}$$

. . . . . .

$$P_{2(i)}^{\cdot} + P^{=} \rightarrow P_2^{\cdot}(i+1)$$

$$P_{2(i+1)}^{\cdot} \xrightarrow[h\nu]{k_5} P^{=} + r$$

$$r^{\cdot} \xrightarrow{k_6} \text{destruction.}$$

Here $P^{=}$ is a polymer molecule containing a double bond, $P_{2(i)}$ is a polymer radical containing i double bonds, and $r^{\cdot}$ is a low-molecular-weight radical.

The calculation of the rate of accumulation of C=C bonds based on this scheme agrees with the empirical equation

$$[P^{=}] = [P^{=}]_{\infty}(1 - e^{-w_0 t/[P^{=}]_{\infty}}),$$

where $[P^{=}]_{\infty} = 1.6$ M and w_0 is the initial rate of formation of C=C bonds and of consumption of ester groups. All the free radicals were recorded by EPR and the regions of their thermal and photochemical stability were investigated.

V. CERTAIN NEW METHODS FOR THE INVESTIGATION OF FREE RADICALS

The wide-scale application of EPR in the chemical physics of polymers is in most cases limited by the difficulties associated with the elucidation of the complex EPR spectra of real polymer specimens. Although modern quantum chemistry and the use of computers make it possible to obtain information from the analysis of EPR signals, in the case of specially complex signals or spectra consisting of a superposition of signals due to different chemical centres, the methods of theoretical analysis are relatively ineffective [86].

The EPR signals of the vast majority of organic free radicals have virtually the same g-factor in the region $g_0 \simeq 2$, by differing $\Delta g \simeq 10^{-4}-10^{-5}$. The distance between the centres of such signals in units of the magnetic field $\delta H \simeq \Delta g H_0/g_0$ is approximately 1 G in the usual EPR spectrometers ($H_0 \simeq 3 \times 10^3$ G; 3 cm range). On the other hand, the intrinsic line width of organic radicals in polymers is not less than 3–10 G, so that the signals are usually superimposed.

Submillimetre EPR spectroscopy was used recently for the first time to investigate free radicals [87]. The magnetic field strength in such a spectrometer reaches 50 000 G (2 mm range). The distance between the signals of organic radicals is then found to be 10–20 G (on average 15 times greater than in the usual microwave spectrometer) and it is possible to record and analyse the spectra of individual radicals.

Fig. 17 presents the EPR spectra of macroradicals in polytetrafluoroethylene γ-irradiated in the presence of oxygen and then kept in the light [88]. It is evident that, in contrast to the EPR spectrum belonging to the usual 3 cm range, which contains relatively little information, the spectrum in the 2 mm range makes it possible to distinguish terminal alkyl, allyl, and terminal peroxy-radicals. Fig. 17*b* shows that the new method makes it possible to distinguish even terminal and central peroxy-radicals.

Thus there is a unique possibility of investigating the kinetics of complex free radical processes involving several kinds of free radicals.

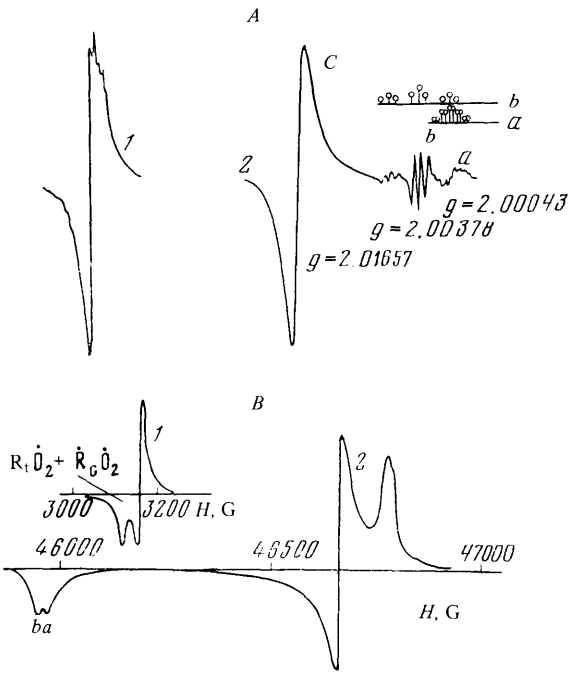


Figure 17. Comparison of the EPR spectra of polytetrafluoroethylene radicals obtained with the aid of 3 cm (curve *1*) and 2 mm (curve *2*) microwave spectrometers: *A*) allyl radicals (*a*), alkyl radicals (*b*), and peroxy-radicals (*c*); *B*) central R_cO_2 radical (a) and terminal R_tO_2 radical (b).

Under the real conditions in the ageing of polymers, the concentrations of the free radicals formed in the latter are too low to be detected by EPR. The application of the spin-trapping method is therefore apparently promising in this connection. The method has been used successfully in recent times for the investigation of radical processes in the liquid phase [89–91].

The principal idea of the spin trapping method consists in the conversion of an active short-lived radical $r^{\cdot}$ as a result of its addition to a specially selected acceptor T (spin-trapping agent) into a much more stable radical $rT^{\cdot}$ (the spin adduct):

$$r^{\cdot} + T \xrightarrow{k_1} rT^{\cdot}.$$

The latter can be accumulated in concentrations sufficient for its detection by EPR. In order to estimate the ratio of the steady-state concentrations of the active radical (in the absence of T) in the spin adduct, we shall consider the simplest kinetic scheme for the transformations of the

radicals in the presence of T:

$$\text{Initiation} \xrightarrow{w_i} r^{\cdot},$$
$$r^{\cdot} + r^{\cdot} \xrightarrow{k_t} \text{products},$$
$$r^{\cdot} + T \xrightarrow{k_1} rT^{\cdot},$$
$$r^{\cdot} + rT^{\cdot} \xrightarrow{k_t'} \text{products},$$
$$rT^{\cdot} + rT^{\cdot} \xrightarrow{k_t''} \text{products}.$$

In the absence of the spin-trapping agent the stationary concentration of the active radicals is

$$[r^{\cdot}]_{st} = \sqrt{w_i/k_t}. \quad (29)$$

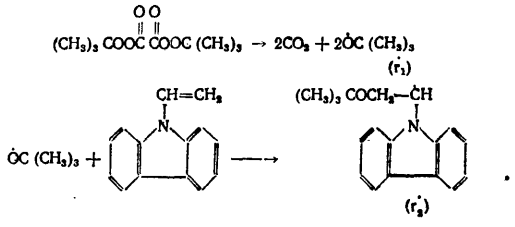
In the presence of a sufficient concentration of the spin-trapping agent $\{k_1[T] \gg k_t[r^{\cdot}]\}$, in the case where the spin adduct is sufficiently stable $\{k_t''[rT^{\cdot}] \ll k_t[r^{\cdot}]\}$, we have

$$[rT^{\cdot}]_{st} = \frac{k_1}{k_t'}[T]. \quad (30)$$

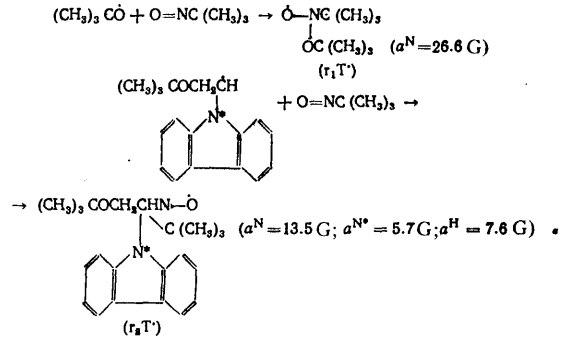
For low rate of initiation, we usually have $[rT^{\cdot}]_{st} \gg [r^{\cdot}]_{st}$.

The spin-trapping method not only makes it possible to detect free radicals, but, by analysing the EPR spectra of the spin adducts, one can determine the nature of the active radicals r$^{\cdot}$ combined. Various compounds with multiple bonds are used as spin-trapping agents—mainly nitroso-compounds and nitrones as well as thiocarbonyl compounds, nitro-compounds, quinones, acetylene derivatives, nitrile *N*-oxides, etc.

As an example we shall consider the results of the investigation by the spin-trapping method of the mechanism and kinetics of the polymerisation of *N*-vinylcarbazole initiated by di-t-butyl peroxyoxalate[89]:



In the presence of 2-methyl-2-nitrosopropane (T) the active radicals $r_1^{\cdot}$ and $r_2^{\cdot}$ add to the spin-trapping agent and give rise to two types of spin adducts $r_1T^{\cdot}$ and $r_2T^{\cdot}$ with markedly different EPR spectra (Fig. 18):



Analysis of the EPR spectrum of the spin adduct $r_2T^{\cdot}$ indicates the direction of the reaction involving the addition of the initiator radical to the monomer.

VI. RELATION BETWEEN THE CHANGES IN THE PROPERTIES OF POLYMERS OF PRACTICAL IMPORTANCE AND THE KINETICS OF AGEING

On the basis of individual elementary reactions, it is now possible to determine the complete process mechanism and to describe the kinetics of the variation of polymer properties of practical importance under any operating conditions.

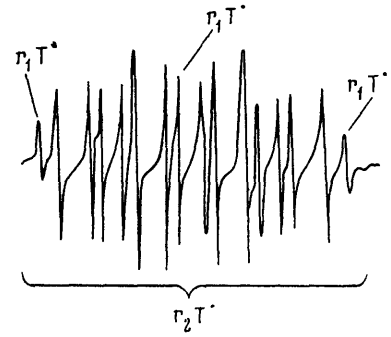


Figure 18. EPR spectrum recorded in the polymerisation of *N*-vinylcarbazole (0.52 M) initiated by di-t-butyl peroxyoxalate (4.3×10^{-2} M) in the presence of 2-methyl-2-nitrosopropane (2.3×10^{-2} M) as the spin-trapping agent; solvent—*p*-xylene; 25 °C.

The mechanism of the photochemical oxidation of polyolefins (ПН) has been investigated in greatest detail[92]. This process is a chain reaction with degenerate photobranching by the hydroperoxide and quadratic chain termination. The mechanism of the photochemical oxidation can be formulated as follows in a general form:

$$\text{ПН} \xrightarrow{h\nu} \rightarrow \text{ПО}_2^{\cdot}$$
$$\text{ПО}_2^{\cdot} + \text{ПН} \xrightarrow[k_p]{O_2} \text{ПООН} + \text{ПО}_2^{\cdot} \text{ — chain propagation},$$
$$\left.\begin{aligned} \text{ПООН} &\xrightarrow{h\nu} \text{ПО}^{\cdot} + {}^{\cdot}\text{ОН} \rightarrow 2\text{ПО}_2^{\cdot} \\ [\text{C=O}] &\xrightarrow{h\nu} f\text{ПО}_2^{\cdot} \end{aligned}\right\} \text{chain branching},$$
$$\text{ПО}_2^{\cdot} + \text{ПО}_2^{\cdot} \xrightarrow{k_t} [\text{C=O}] \text{ — chain termination}.$$

Here [C=O] represents carbonyl compounds, f is the probability of the formation of its free radical in the [C=O]-photochemical decomposition step.

The following system of differential kinetic equations corresponds to this scheme:

$$\left.\begin{aligned} \frac{d[\text{ПО}_2^{\cdot}]}{dt} &= 2\alpha[\text{ПООН}] - k_t[\text{ПО}_2^{\cdot}]^2 + \alpha' f[\text{C=O}]; \\ \frac{d[\text{ПООН}]}{dt} &= k_p[\text{ПН}][\text{ПО}_2^{\cdot}] - \alpha[\text{ПООН}]; \\ \frac{d[\text{C=O}]}{dt} &= \alpha[\text{ПООН}] - \alpha'[\text{C=O}] + \frac{k_t}{2}[\text{ПО}_2^{\cdot}]^2, \end{aligned}\right\} \quad (31)$$

where α and α' are the probabilities of the photochemical decomposition of the hydroperoxide and carbonyl compounds, which are defined by the following relation for thin

specimens:

$$\alpha = \int \varphi\varepsilon(\lambda) I(\lambda)\, d\lambda; \qquad (32)$$

where $\epsilon(\lambda)$ is the absorption spectrum of the decomposing compound, φ the decomposition quantum yield, and $I(\lambda)$ the spectrum of the radiation incident on the specimen.

In terms of dimensionless coordinates, the system of equations is

$$\left.\begin{aligned}
&\frac{d\rho}{d\tau} = (\pi - 4\rho^2 + k_2 fK)\, k_1;\\
&\frac{d\pi}{d\tau} = \rho - \pi/2;\\
&\frac{dK}{d\tau} = 2\rho^2 - k_2 K + \frac{\pi}{2};\\
&\rho = k_t [\Pi O_2^\cdot]/4k_p [\Pi H];\ \pi = [\Pi OOH]/[\Pi OOH]_\infty;\ K = [C{=}O]/[\Pi OOH]_\infty;\\
&k_1 = k_p [\Pi H]/2\alpha;\ k_2 = \alpha'/2\alpha;\ \tau = 2\alpha t;\\
&[\Pi OOH]_\infty = 2k_p^2 [\Pi H]^2/k_t\alpha.
\end{aligned}\right\} \qquad (33)$$

It follows from Eqns. (33) that, under quasi-stationary conditions with respect to $[\Pi O_2^\cdot]$, for different light intensities, and for the same spectral composition, the process kinetics should be described by a single relation in terms of the variables $[C{=}O]/[\Pi OOH]_\infty$ and αt. Fig. 19 illustrates the logarithmic form of this relation calculated using the rate constants for the elementary reactions determined independently. The experimental data fit satisfactorily on the calculated curve [93].

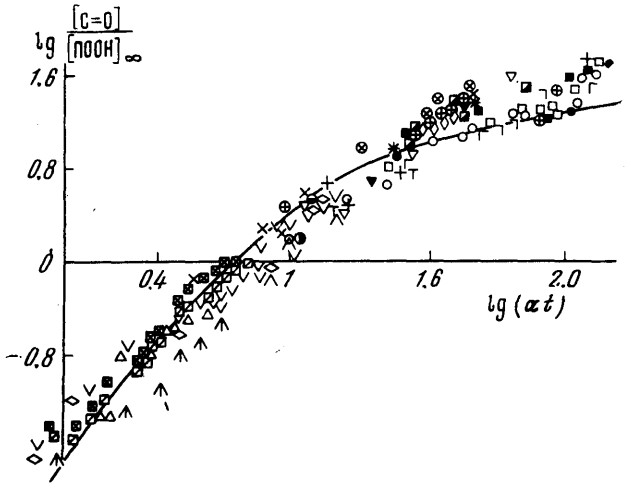


Figure 19. Logarithmic forms of the kinetic curves for the accumulation of carbonyl compounds in the photochemical oxidation of various polypropylene specimens; continuous line—calculation.

When polymeric materials are used in practice, an important factor is not the kinetics of the accumulation of the polymer oxidation products, but the change in characteristics of practical importance, for example, physicomechanical characteristics, the relative elongation on rupture, the tensile strength, etc. These characteristics are not unambiguously related to the composition of the polymer and depend to a large extent on its physical structure. It has been shown for the photochemical oxidation of polypropylene that the change in these characteristics is determined by the kinetics of the chemical reactions occurring in the polymer.

Fig. 20 illustrates the kinetic curves for the variation of the relative elongation on rupture (ϵ, %) in the course of the photochemical oxidation of various polypropylene specimens. Despite the fact that these curves are of different forms, they nevertheless have one feature in common: the change in the relative elongation on photochemical oxidation depends only on the amount of light incident on the polymer and not on its intensity; for high light intensities, the change in the properties takes place less effectively [93]. This is due to the fact that, in the case of quadratic chain termination for low light intensities, the effective oxidation chain length is greater than for high light intensities. Accordingly, at low light intensities there is a high yield of the branching product—the hydroperoxide, as a result of which all the degradation processes per quantum of the incident light take place more effectively.

The relations obtained for different light intensities can be combined into a single one if the number of radicals Ω formed in the polymer during oxidation, and not the amount of light incident on the polymer, is plotted along the abscissa axis (Fig. 2). In conformity with this mechanism, the number of radicals is determined as the sum of the steps involving the photochemical decomposition of the branching products—hydroperoxides and carbonyl compounds:

$$\Omega = \int_0^t (2\alpha [\Pi OOH] + f\alpha' [C{=}O])\, dt. \qquad (34)$$

Sometimes, for example, in the case of oriented polypropylene or polypropylene thermally stabilised by phenols, Ω can be calculated even if the overall kinetic mechanism of the photochemical process is unknown. This makes it possible to describe the kinetics of the change in the mechanical properties of polypropylene when the process mechanism is not completely known.

Thus the dynamics of the change in the physicomechanical properties of the polymer is related to the kinetics of the chemical ageing process and calculations on such dynamics can be performed on the basis of the measurement of its kinetic characteristics.

VII. PRINCIPLES OF THE STABILISATION OF POLYMERIC MATERIALS FROM THE STANDPOINT OF THE MECHANISM OF AGEING

The known methods for the stabilisation of polymeric materials can be divided in accordance with the stage of the ageing process on which they act (Table 3). The simplest procedure involves the mechanism of the action of stabilisers which prevent the initiation of ageing. These are, for example, waxes and coatings which prevent the penetration of chemical agents into the polymer and photoabsorbers—substances which absorb photochemically active light. Such stabilisers act in the surface layer of the polymeric material.

Substances which reduce the probability of the formation of an active centre in the initiation stage constitute a large group of stabilisers. These include agents which quench excited states ("quenchers")—substances which

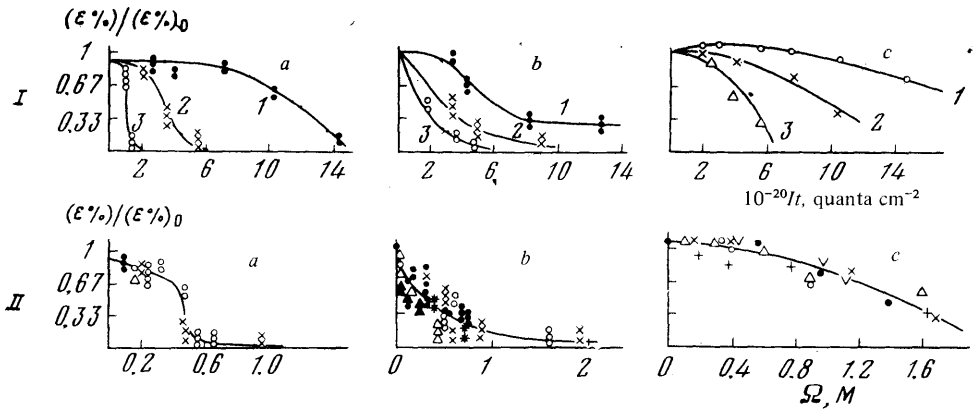


Figure 20. Variation of the relative elongation on rupture (ϵ, %) for polypropylene in the course of its photochemical oxidation: I) dependence on the light It incident on the specimen; II) dependence on the dose Ω of the radicals formed in the specimen in a given period; *a*) isotropic specimen; *b*) oriented annealed specimen; *c*) oriented specimen (950%). Light intensity $\eta = 254$ nm: 1) $\times 10^{15}$ quanta cm^{-2} s^{-1}; 2) 0.7×10^{15} quanta cm^{-2} s^{-1}; 3) 0.24×10^{15} quanta cm^{-2} s^{-1}.

react with various admixtures catalysing the decomposition of polymers. Stabilisers which deactivate chemically active reaction products, for example, substances which decompose hydroperoxides (the branching products of the chain thermal oxidation process) are of particular importance.

Stabilisers which influence the stage involving the development of the ageing process, for example, the oxidation chain propagation stage, include substances which prevent the penetration of oxygen into the polymeric material or reduce its concentration in the material. In the absence of oxygen the chemical composition of the product arising in the chain propagation stage changes, unstable branching products are not formed, and the ageing process is retarded. As an example of such stabilisers, one may quote finely dispersed metals and substances giving rise to them, which are used as stabilisers of thermostable materials [94].

The class of stabilisers which accelerate the stage involving the destruction of active centres, for example, free radical acceptors or inhibitors of free radical process InH are most widely used in practice and have been studied in greatest detail. By interacting with active radicals, they lead to the formation of relatively inactive inhibitor radicals In$^{\cdot}$.

The antiradical activity of such inhibitors (stabilisers) is usually characterised by the rate constant for their interaction with the active radical (k_7). [95] Their efficiency is determined also by the activity of the radical In$^{\cdot}$, which is characterised by the ratio k_{10}/k_p of the rate constants for the reactions

$$RO_2^{\cdot} + RH \xrightarrow{k_p} ROOH + R^{\cdot} \quad ,$$

$$In^{\cdot} + RH \xrightarrow{k_{10}} InH + R^{\cdot} \quad .$$

The lower this ratio the greater the inhibiting effect of the inhibitor.

In the thermal oxidation of polymers the practical efficiency of active radical acceptors is not only determined by the constants k_7 and k_{10} but depends also on the possibility of the additional initiation of the ageing process as a result of the interaction of the radical In$^{\cdot}$ with the hydroperoxide [96] and the decomposition of the quinolide peroxides formed in the reaction of the active radical with the stabiliser radical [97].

The set of these factors is taken into account in a special automated method for testing chemical compounds for their suitability as stabilisers of polymeric materials, which was developed recently in the Sector of the Kinetics of Chemical and Biological Processes of the Institute of Chemical Physics of the USSR Academy of Sciences. The measuring system includes a highly sensitive differential manometric apparatus with continuous recording of the rate of oxidation. At the same time the experimental data are automatically transmitted via a communication link to a BESM-6 computer, where they are interpreted. The mathematical solution of the problem consists of two dialogues incorporating approximately ten programs for the treatment of the data. The investigator controls the treatment directly from the laboratory via a "Videoton-340" display. Both the intermediate and final results of the calculations are displayed on the Videoton screen. The results are presented in the form of Tables and graphs executed with the aid of external devices of the computer. For control and storage, the initial information is coded by means of a Teleprinter on perforated tape. The system is designed for the simultaneous operation of four experimental sets of apparatus.

VIII. A NEW EFFECTIVE METHOD FOR THE STABILISATION OF POLYMERS—A "DEPOT" OF STABILISERS

Many stabilisers cannot be used at the required concentrations for different reasons. For example, certain stabilisers impart an undesirable colour to the polymeric material and thermal stabilisers can prove to be also effective photosensitisers. Free radicals formed from the stabilisers in some cases enter into reactions which promote the decomposition of the polymer. Furthermore, the stabiliser can be consumed in useless side reactions.

It is therefore desirable to create stabilising compositions in such a way that the effective inhibitor acts in accordance with the principle of *in statu nascendi*, i.e. that its main bulk should remain in the bound state, a kind of "depot", and that the active form of the stabiliser is released from the latter gradually or when necessary. A quantitative criterion of the effectiveness of the inhibitor *in statu nascendi* can be found by analysing a simplified kinetic scheme for the action of such inhibitors Z on an initiated chain process:

$\xrightarrow{w_i}$ r· — initiation of active radical;

Z $\xrightarrow{k}$ R· — the formation of a "depot" of the active form of the inhibitor R which functions as the stabiliser (for simplicity, a stabiliser in a radical form is considered);

R· + r· $\xrightarrow{k_7}$ — inhibition reaction;

R· $\xrightarrow{k_{10}}$ r· — regeneration of the active radical via a reaction with participation of the inhibitor.

If the concentration of the stabiliser is fairly high and the active centres are destroyed only on interaction with it, then the efficiency of the stabilisation by such a stabiliser can be characterised by the ratio of the rates of initiation and consumption of the active form of the inhibitor:

$$\psi = \frac{w_i}{d[\dot{R}]/dt} \simeq \frac{w_i}{k[Z]} \quad (\text{when } k_{10} \gg k). \tag{35}$$

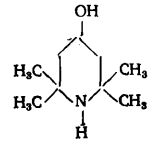
If an inhibitor is introduced initially at a concentration $[Z]_0$, then its efficiency ψ is defined by the expression

$$\psi_0 = \frac{w_i}{w_i + 2k_{10}[Z]_0}. \tag{36}$$

Since by hypothesis $k_{10} \gg k$, it follows that $\psi > \psi_0$. The ratio $\psi/\psi_0 = Q$ can serve as a criterion of the usefulness of the inhibitor *in statu nascendi*:

$$Q = \frac{\psi}{\psi_0} = \frac{w_i + 2k_{10}[Z]_0}{k[Z]_0} \simeq \frac{2k_{10}}{k}. \tag{37}$$

It has been shown recently that sterically hindered piperidines protect polymers from the action of light via the "depot" mechanism[98]. The mechanism of their light stabilising activity remained obscure for a long time. In the literature it was only noted that these compounds should not act via any one of the known mechanisms. In reality it was found that the stabilisers are not the piperidines themselves, being converted in the course of the ageing of the polymer into a mixture of nitroxy-radicals and other compounds which act as inhibitors. Fig. 21*a* presents kinetic curves for the photochemical oxidation of the butadiene–acrylonitrile copolymer. The initial section of the kinetic curve *2* for the oxidation in the presence of 2,2,6,6-tetramethyl-4-hydroxypiperidine



coincides with the curve for the unstabilised specimen (curve *1*) and the rate of oxidation falls only after some time has elapsed. During this period, stabile nitroxy-radicals accumulate in the specimen (curve *3*). The introduction into the polymer of a mixture of piperidine and radicals lowers the rate of the photochemical oxidation process from the very beginning. The addition to the polymer of nitroxy-radicals alone at the same concentration has little influence on the oxidation kinetics owing to the rapid consumption of the stable radicals.

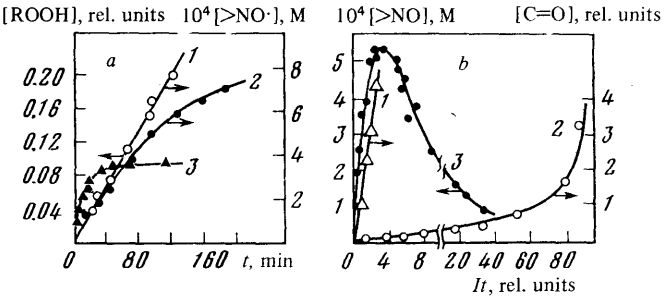


Figure 21. Kinetic curves for photochemical oxidation in the presence of 4-hydroxy-2,2,6,6-tetramethylpiperidine (NH); λ = 280 nm: *a*) butadiene–acrylonitrile copolymer (SKN-26). Accumulation of alcohols: 1) without stabiliser; 2) 2×10^{-1} M NH; 3) accumulation of NO in the specimen containing 2×10^{-1} M NH; *b*) polypropylene. Formation of carbonyl compounds: 1) without stabiliser; 2) 3.2×10^{-2} M NH; 3) variation of the concentration of NO.

The mechanism of the stabilising action of sterically hindered piperidines is more complex than that considered above. It can be described qualitatively as follows:

$\xrightarrow{w_i}$ r· — photoinitiation;

>NH $\xrightarrow{+\dot{r}, +rO_2}$ >NO· + r· — generation of the stabiliser and the active radical;

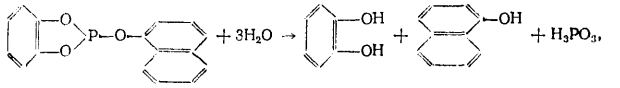
>NO + r· → S
S + rO₂· → >NO₂ — inhibition and regeneration of stabiliser;

>NO· $\xrightarrow{h\nu}$ r· — generation of active radicals.

Here S is an intermediate product. The stage of the generation of the stabiliser involving the formation of nitroxy-radicals >NO·, which can proceed with participation of singlet oxygen or peroxy-radicals, and the reactions involving the regeneration of the active form as a result of the apparent conversion of the nitroxy-radical into hydroxylamine and an ether from which the nitroxy-radical can be reformed in its turn, are important. The possibility of the regeneration of the inhibitor of the system makes piperidines and nitroxy-radicals extremely effective polymer stabilisers.

Fig. 21*b* shows how the concentration of the nitroxy-radical formed from sterically hindered piperidine changes in the course of the photochemical oxidation of polypropylene. Evidently, throughout the reaction period, the concentration of nitroxy-radicals in the specimen is lower almost by two orders of magnitude than the initial concentration of piperidine. The introduction of nitroxy-radicals into the polymer at a high concentration at the beginning of the process is in the present instance undesirable owing to

the development of an intense colour in the specimen. The function of a "depot" can also be fulfilled by phosphite esters, whose hydrolysis leads to the formation of the corresponding phenols or catechols[99]:



as well as clathrate compounds from which the stabiliser is liberated on thermal or photochemical decomposition.

Not only compounds from which the stabiliser is synthesised during ageing but also the undamaged portion of the polymer from which the stabiliser diffuses to the degradation zone can be used as a "depot" of stabilisers. This phenomenon was recently observed in a study of the photochemical oxidation of polybutadiene films.

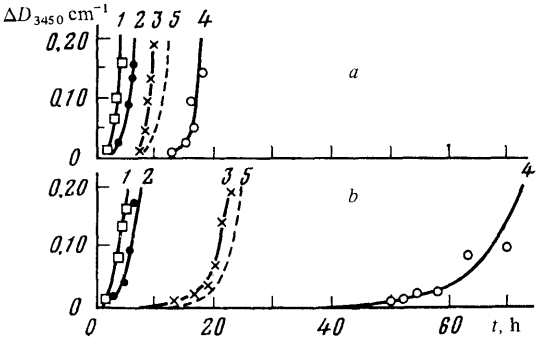


Figure 22. Kinetic curves for the photochemical oxidation of polybutadiene films 20 μm (*a*) and 60 μm (*b*) thick, without additives (curve *1*) and stabilised by additives; 2) 4-heptyloxy-2-hydroxybenzophenone UVA (3.6×10^{-2} M); 3) 2,6-di-t-butyl-4-methylphenol A (5×10^{-2} M); 4) their mixture with the same UVA and A concentrations (wavelength 254 nm); 5) calculated curves for films containing a mixture of UVA and an antioxidant corresponding to their additive activity.

In the presence of a u.v. absorber, light does not penetrate into the bulk of the polymeric specimen. Photochemical oxidation takes place only in the surface layer, which results in the consumption of the antioxidant (A). The concentration gradient of A rises and the antioxidant diffuses from the bulk of the polymer to the surface layer. Since deep layers serve as a source of the inhibitor, thick specimens are oxidised more slowly than thin specimens (Fig. 22). It has been shown recently that this phenomenon is the principal cause of the synergism observed in the stabilisation of polymers by mixtures of u.v. absorbers (UVA) and antioxidants, which interact with free radicals[100,101].

The problem of the influence of diffusion of A on the duration of the induction period in the oxidation reaction (T_{ind}) has been solved[101] for the unbranched chain photochemical oxidation reaction via the mechanism

$$S + h\nu \xrightarrow{PH,\ O_2} P\dot{O}_2 \quad ,$$

$$P\dot{O}_2 + PH \xrightarrow{k_2} POOH + P\dot{O}_2 \quad ,$$

$$P\dot{O}_2 + P\dot{O}_2 \xrightarrow{k_3} \text{chain termination},$$

$$P\dot{O}_2 + A \xrightarrow{k_4} \text{chain termination}.$$

Here S is the photosensitiser. The system of diffusion-kinetic equations describing the kinetics of the consumption of A and of the formation of $P\dot{O}_2$ in different sections of the polymer (x) during the induction period is as follows:

$$\left.\begin{aligned}
&\frac{\partial [PO_2(x,t)]}{\partial t} = -k_4 [A(x,t)]\,[PO_2(x,t)] + w_0 e^{-\alpha x} + D_{PO_2} \frac{\partial^2 [PO_2(x,t)]}{\partial x^2}\ ;\\
&\frac{\partial [A(x,t)]}{\partial t} = -k_4 [A(x,t)]\,[PO_2(x,t)] + D_A \frac{\partial^2 [A(x,t)]}{\partial x^2}\ ;\\
&0 < x < l;\ 0 < t < T_{ind};\\
&[PO_2(x,t)]_{t=0} = 0;\ [A(x,t)]_{t=0} = [A]_0;\\
&\frac{\partial [A(x,t)]}{\partial x}\Big|_{x=0} = \frac{\partial [PO_2(x,t)]}{\partial x}\Big|_{x=0} = 0;\\
&\frac{\partial [A(x,t)]}{\partial x}\Big|_{x=l} = \frac{\partial [PO_2(x,t)]}{\partial x}\Big|_{x=l},
\end{aligned}\right\} \quad (38)$$

where $\alpha = [A]_\epsilon$ is the UVA absorption index, D_i the diffusion coefficient, l the film thickness, and w_0 the rate of formation of free radicals on the surface of the film (for $x = 0$). The characteristic reaction conditions obtained by solving Eqns. (38) are illustrated in Figs. 23*a* to 23*c*.

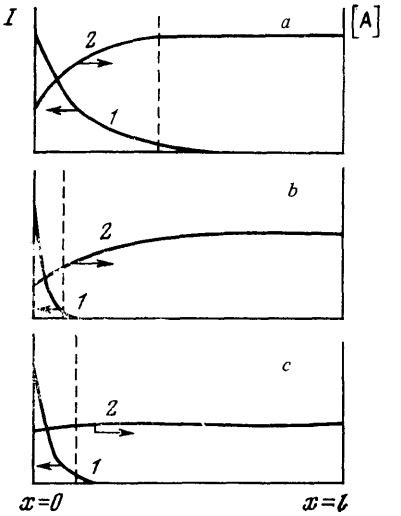


Figure 23. Distribution of light intensity (curve *1*) and antioxidant concentration (curve *2*) in the thickness of a polymer film for photochemical oxidation processes under different conditions: *a*) static; *b*) diffusion-controlled; *c*) rapid diffusion. The dashed line indicates the section in which the reaction is 20 times slower than on the surface. The photochemical reaction zone is located between this line and the surface ($x = 0$).

Under local conditions ($T_{ind} \ll l^2/\pi^2 D_a$, $T_{ind} \ll \alpha^2 l^4/\pi^2 T_A$), we have

$$T_{ind} = a[A_0]/I,$$

where I is the light intensity and a a constant. During the period T_{ind}, the diffusion of A is very slight and does not affect T_{ind}. Each layer reacts independently. The distribution of A in the film thickness at time t is therefore determined by the distribution of light intensity (Fig. 23*a*).

Under diffusion-controlled conditions ($1/\pi^2 D_A \alpha^2 \ll T_{ind} \ll l^2/\pi^2 D$, $\alpha l \gg 1$), we have

$$T_{ind} = bD_A \alpha^2 [A]_0^2/I^2. \quad (39)$$

In contrast to the local conditions, under these conditions there is an exchange of the antioxidant between neighbouring layers. As a result, $+d[A]/dt$ varies more smoothly than I along the thickness of the film (Fig. 23*b*).

Under rapid diffusion conditions ($T_{ind} \gg l^2/\pi^2 D_A$, $T_{ind} \gg 1/\pi^2 L_A \alpha^2$), we have

$$T_{ind} = a[A]_0 \alpha l/I, \quad (40)$$

i.e. [A] is virtually constant throughout the thickness of the film (Fig. 23*c*). Under these conditions, as under local conditions, the kinetics of the transformation of A are independent of D_A. T_{ind} is greater than under local conditions by a factor of αl. This is the maximum synergistic effect within the framework of the diffusion mechanism.

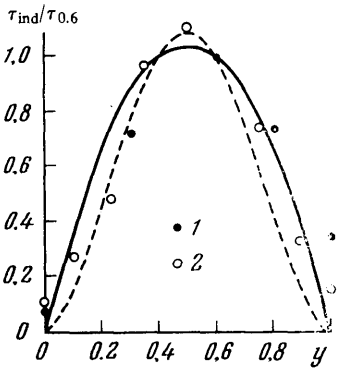


Figure 24. Dependence of the relative induction periods for the oxidation reaction $T_{ind}/\tau_{0.6}$ ($\tau_{0.6}$ is the induction period for $y = 0.6$) on the fraction of A: 1) in a mixture of 2,6-di-t-butyl-4-methylphenol and 4-heptyloxy-2-hydroxybenzophenone on irradiation of polybutadiene films 60 μm thick with light at 254 nm ($c\Sigma = 8.6 \times 10^{-2}$ M); 2) in a mixture of 2,2-methylenebis-(6-t-butyl-4-methylphenol) and 2-hydroxy-4-octyloxybenzophenone on irradiation of polychloroprene films[102]. Curves—calculation by Eqn.(41) (continuous curve) and by Eqn.(42) (dashed curve), normalised with respect to the experimental point corresponding to $y = 0.6$.

Analysis[100,101] showed that, for specified A and UVA concentrations, the synergistic effect can depend on I, D_A, and l, and the existence of such relations has been confirmed experimentally. The diffusion mechanism also made it possible to obtain the dependence of T_{ind} on the composition of the mixture of stabilisers. Under rapid diffusion conditions, we have

$$T_{ind} \sim c_\Sigma y(1-y) \quad (41)$$

and under diffusion-controlled conditions

$$T_{ind} \sim [c_\Sigma y(1-y)]^2, \quad (42)$$

where $c\Sigma$ is the overall concentration of stabilisers and y the mole fraction of A in the mixture. Fig. 24 shows that Eqns. (41) and (42) reflect correctly, in qualitative terms, the form of the dependence of T_{ind} on the composition of the synergistic mixture.

Thus the diffusion mechanism explains the observed dependence of the synergistic effect on the composition of the mixture of stabilisers, I, D_A, and α. The principles of the selection of synergistic mixtures for different polymers and different operating conditions as well as the requirements which must be met by the thicknesses of the specimens and the conditions under which the tests of the resistance to light by polymers stabilised with synergistic mixtures have to be accelerated acquire theoretical justification. On the basis of this mechanism, the resistance to light will be presumably significantly influenced by the irradiation conditions. Under conditions of periodic irradiation, the synergistic effect will be greater than under conditions of continuous irradiation; in particular, an increased resistance to light should be promoted by the nightly interruption of irradiation. During the night, diffusion will increase [A] in the surface zone of the polymer where [A] was consumed during the day. It is also possible to account for the synergism between the effect of the UVA and substances causing a non-radical decomposition of hydroperoxides. On the basis of the diffusion mechanism, a quantitative mechanism of the synergistic effect is possible.

IX. THE AGEING OF POLYMERS UNDER SPECIAL OPERATING CONDITIONS

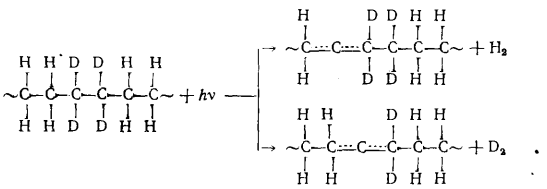
1. The Influence of Vacuum Ultraviolet Radiation on Polymers

In Space, a polymeric material is acted upon by vacuum ultraviolet (v.u.v.) radiation ($\lambda < 200$ nm). Such radiation constitutes a significant proportion of the spectrum of solar radiation, but does not reach the surface of the Earth, since it is absorbed by the ozone layer of the atmosphere.

The degradation of polymers under the influence of the v.u.v. differs from that under the influence of the softer u.v. with $\lambda > 200$ nm as well as the harder γ-radiation[103-106]. For example, polyolefins scarcely absorb light at a wavelength $\lambda > 200$ nm and their photodegradation under the influence of radiation in this spectral region therefore proceeds as a result of the absorption of light by impurities, which play the role of photosensitisers. The action of γ-rays on polyolefins is determined by the comparatively slow secondary electrons, which generate positively charged ions, free electrons, and excited molecules in the singlet and triplet states in the given substance. Secondary processes give rise to hydrogen atoms and free macroradicals, which initiate the radical degradation of the polymer.

The absorption maximum of polyolefins lies in the v.u.v. region. As a result of the absorption of a quantum of v.u.v. light with an energy insufficient for photoionisation, a polyolefin (polyethylene) molecule is transformed to an excited singlet state (in contrast to γ-radiolysis, the

probability of the formation of triplet molecules is extremely small). This state is unstable and the molecule decomposes mainly into molecular hydrogen and a polymer molecule containing a double bond of the *trans*-vinylene type. The hydrogen molecule is apparently abstracted from a single carbon atom, since the fraction of HD in the photolysis ($\lambda = 147$ nm) of the ethylene–deuteroethylene copolymer is small:



2. Degradation of Polymers in the Tissues of a Living Organism

In the last decade polymers have found extensive applications in medicine (cardiovascular surgery, surgery of the internal organs and tissues, traumatology, orthopaedic surgery, blood substitutes, agents prolonging the action of drugs, etc.). On contact with the tissues of the organism, polymeric materials undergo a change in properties to some extent and can influence the vital activity of the organism. The interaction of the polymer with the organism is a many-factor process, the understanding of which requires the investigation of processes involving the decomposition of implanted polymers, the metabolism of the decomposition products of the polymers and additives, and the genetic consequences of the action of polymers and their decomposition products on the organism.

In the general case implanted polymers are involved in three processes.

1. The sorption by the polymer of the components of the surrounding medium (water, salts, proteins, and lipids). For example, the sorption of lipids by cardiac valves made of polyorganosiloxanes leads to failure of the valves.

2. Desorption of low-molecular-weight compounds (catalysts, stabilisers, and fillers) from the polymers.

3. The decomposition of polymers as a result of degradation (thermal and mechanical energy, water, salts, enzymes) and dissolution. For example, the presence of low-molecular-weight oligomers, in equilibrium with the polymer, is characteristic of polycondensation polymers. The dissolution of these oligomers in the surrounding medium decreases the mass of the implanted material.

The macrokinetic features of the decomposition of polymers in the tissues of the living organism have been investigated[107,108]. Two main types of degradation of polymers in the organism are known—on the surface and in the bulk of the implanted material.

For the majority of hydrophobic polymers, the rate of decomposition of chemically unstable bonds under the influence of salts and enzymes greatly exceeds the rate of diffusion of these components in the polymer[107]. The degradation reaction proceeds in the surface of the implanted material at the rate

$$\frac{dn}{dt} = k^S C_m^S C_{cat}^S \cdot S, \qquad (43)$$

where n is the number of unstable bonds which have decomposed and C_m^S and C_{cat}^S are the surface concentrations of the chemically unstable bonds and the catalyst.

In the case of a simple fibre the change in the radius r, the mass m, and the breaking stress σ in the course of degradation, unaccompanied by the cracking of the surface, are described by the equations

$$\frac{r}{r_0} = 1 - k_{eff}^S \frac{t}{r_0 \rho}, \qquad (44)$$

$$\left(\frac{m}{m_0}\right)^{1/3} = \left(\frac{\sigma}{\sigma_0}\right)^{1/3} = 1 - k_{eff}^S \frac{t}{r_0 \rho}, \qquad (45)$$

where $k_{eff}^S = kC_m^S C_{cat}^S$ and ρ is the density of the polymer.

The degradation of poly(ethylene terephthalate) fibres in human subcutaneous cellular tissue has been investigated[108]. Fig. 25*a* shows that relation (45) holds satisfactorily. The experimental data make it possible to predict the time τ of the complete decomposition of the implanted material:

$$\tau = r_0 \rho / k_{eff}, \qquad (46)$$

which in the given instance is 30 ± 3 years.

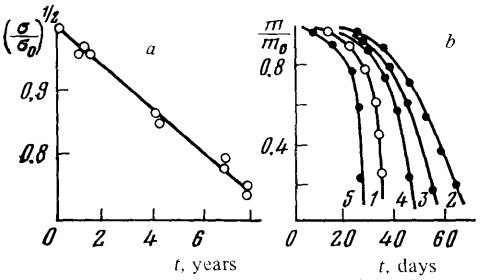


Figure 25. *a*) Variation of the relative breaking stress for a simple poly(ethylene terephthalate) fibre with $r_{init} = 11$ μm on the implantation time in the subcutaneous cellular tissue of man; *b*) kinetic curves for the variation of the mass m/m_0 of a polyglycolide fibre in the subcutaneous cellular tissue of rabbit (curve 1), in water (curve 2), and in phosphate buffer solutions at different concentrations: 1) 0.1 M; 4) 0.5 M; 5) 1.0 M; pH 7.4; 37°C.

In the degradation of the bulk phase of amorphous polymers, where the accessibility of all the chemically unstable bonds is as a rule the same, the degree of conversion with respect to the bonds and with respect to mass varies in accordance with the laws of homogeneous kinetics[107].

In amorphous-crystalline polymers the accessibilities of chemically unstable bonds in the amorphous regions and in the crystallites are different. The degradation of polyglycolide (degree of crystallinity approximately 80%) takes place under kinetic conditions in the amorphous regions and on the lateral surface of the crystallites.

Fig. 25*b* presents kinetic curves for the variation of the degree of conversion with respect to mass in the degradation of polyglycolide filaments in water, phosphate buffers of different concentrations, and in the subcutaneous cellular tissue of rabbits. Evidently phosphate ions greatly accelerate the degradation process and, for example in 1 M solution, the degradation of polyglycolide is faster than in the tissues of the living organism.

The variation of the mass of polyglycolide is described by the equation

$$\frac{m}{m_0} = \varphi_{cr} - \varphi_{am}[1 - \exp(-k_{eff}^{V} c_{cat}^{V} t)]^2 + \varphi_{cr}\left(1 - \frac{k_{eff}^{V-S} c_{cat}^{V-S} t}{N b_0 \rho}\right)^2, \quad (47)$$

where φ_{am} and φ_{cr} are the volume fractions of the amorphous and crystalline phases respectively, k_{eff}^{V} and k_{eff}^{V-S} are the effective rate constants for the degradation in the amorphous regions and on the surface of crystallites with a diameter b_0, and N is the number of crystallites per cross-section of the elementary filament.

The study of the characteristics of the degradation of polymer materials in the living organism makes it possible to predict the time required for the complete decomposition of the implanted materials.

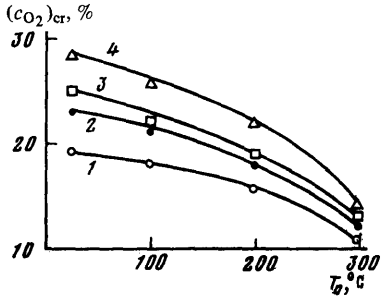


Figure 26. Decrease of the oxygen index $(c_{O_2})_{cr}$ with increase of the initial temperature T_0 of polystyrene specimens with added bromine-containing inhibitor (%): 1) 0; 2) 5; 3) 10; 4) 15.

3. Combustion of Polymers

The extensive use of polymeric materials in the building, textile, furniture, and other industries has greatly increased the importance of the problem of reducing the combustibility of polymers. Many of the commonest polymers—polystyrene, poly(methyl methacrylate), polyurethane, polyethylene, and natural and synthetic rubber—are highly combustible and readily ignite.

In order to estimate the degree of combustibility of the material, it is necessary to determine the conditions under which combustion is stable and the conditions under which it is quenched, i.e. it is necessary to find the critical conditions for combustion. These critical conditions are quoted in the literature: the minimum concentration of oxygen $(c_{O_2})_{cr}$, the minimum size of the specimen d_{cr}, the minimum pressure p_{cr}, the minimum temperature T_{cr}, etc. All these critical conditions are interrelated. For example, Fig. 26 [109] illustrates the decrease of $(c_{O_2})_{cr}$ with increase of the initial temperature of a polystyrene specimen—pure and with added bromine-containing inhibitor.

The oxygen index (OI)—the minimum concentration of oxygen $(c_{O_2})_{cr}$ at which combustion can still occur—is most often used to estimate the combustibility of the material. An advantage of the OI is its satisfactory reproducibility. However, the combustibility of the given material in air is of greatest interest, so that the characteristic based on the change in the composition of the atmosphere is not always suitable.

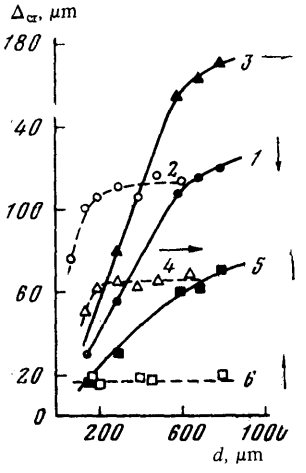


Figure 27. Dependence of the minimum thickness Δ_{cr} of PMMA films on the diameter d of copper wires (curves *1*, *3*, and *5*) and glass fibres (curves *2*, *4*, and *6*) in combustion from above downwards (curves *1* and *2*), horizontally (curves *3* and *4*), and from below upwards (curves *5* and *6*).

Table 8. Conditions for the quenching of the combustion of polymer films [poly(methyl methacrylate) on copper wire and glass fibres]. Test of the applicability of the Zel'dovich–Peclet number to polymer films.

Support	Direction of combustion	d, μm	Δ_{cr}, μm	w_{cr}, cm s^{-1}	L, cm	$10^5(dm/dt)_{cr}/\Delta_{cr}$, g cm s^{-1}
Copper	from above downwards	150	30	1.29	0.19	7.2
		300	55	0.70	0.30	8.3
		700	115	0.35	0.64	8.6
	horizontally	150	40	1.31	0.29	8.6
		300	80	0.70	0.53	10.0
		700	165	0.36	1.23	9.4
Glass	from above downwards	250	110	0.30	0.37	11.6
		350	110	0.21	0.29	10.3
		500	110	0.16	0.23	9.9
	horizontally	250	65	0.64	0.34	9.4
		350	65	0.46	0.32	7.2

Combustibility can be characterised by the minimum size of the specimen capable of combustion. This criterion is widely used for gaseous systems (particularly in the design of fire breaks), but is more rarely employed in the combustion of polymers. Fig. 27 and Table 8 illustrate the dependence of the minimum thickness Δ_{cr} of PMMA films on copper wires and glass fibres on the diameter d of the wire or fibre for different orientations of the specimen [110]. These results are of interest for the study of the combustion of insulating coatings on electric wires and also for the combustion of glass plastics. With increase of

the diameter of the wire, the quantity Δ_{cr} initially increases rapidly and then the relation $\Delta_{cr}(d)$ is weakened. For glass fibres, the $\Delta_{cr}(d)$ curves has a plateau. It might have been expected that thinner films would be capable of combustion on glass fibres than on copper wires. However, this is true only for a large diameter; for small values of d, thinner films can actually burn on copper than on glass. This is due to the fact that, for large diameters of the wire, the copper support removes heat from the burning polymeric films more effectively than the glass support and, for small values of d, the dominant factor is the supply of heat from the flame to the polymer via the wire.

By analogy with the Zel'dovich criterion for the quenching of homogeneous gaseous mixtures,

$$Pe = Pe_{cr} = ud_{cr}/a_T = \text{const} \quad (48)$$

(where Pe is the Peclet number, d_{cr} the critical diameter of the tube, a_T the thermal diffusivity of the fresh mixture, and u the linear rate of combustion), it was shown [110] that the product

$$\dot{m}_{cr} \cdot \Delta_{cr} = \rho w_{cr} \frac{\Delta_{cr}}{L}, \quad (49)$$

where m_{cr} and w_{cr} are the critical mass and linear rate of combustion, ρ the density of the polymer, and L the length of the pyrolysis zone (the distance from the flame barrier to the section where the film is fully gasified) can be used as a quantity characterising the stability of the combustion of polymer films. It follows from Table 8 that, when the thermal diffusivity of the support changes by more than two orders of magnitude (copper–glass) and the diameter of the wire (fibre) changes by a factor of 5, the quantity Δ_{cr} changes by a factor of 5.5, w_{cr} changes by a factor of 8, and the product $M_{cr}\Delta_{cr}$ changes only by a factor of 1.6.

The combustion of a polymer in a centrifuge has been studied [111]. Here the load factor a can serve as a critical parameter. It was observed that in the propagation of the flame along the acceleration vector, the ignition of paper takes place at an acceleration $a_{cr} = 5g$; on the other hand, if the flame is propagated in the opposite direction, ignition occurs at a much higher acceleration ($a_{cr} = 100g$), since in this case the hot combustion products flow in the direction of the propagation of the flame and heat ahead of the combustion front.

The knowledge of the critical combustion conditions makes it possible to arrange polymeric materials in a series based on decreasing combustibility with a particular degree of reliability. Only few polymeric materials have a low combustibility and do not require the addition of combustion inhibitors. Such materials include Teflon, rigid poly(vinyl chloride) (PVC) as well as synthetic fibres—Cordelan [based on PVC and poly(vinyl alcohol)] Nomex, and Kevlar (based on aromatic amine polymers).

However, for the majority of polymeric materials, the problem of the reduction of combustibility still remains extremely urgent. It is fairly difficult, since an increase of fire resistance usually has a number of undesirable consequences. For example, the majority of combustion inhibitors increase the toxicity of the combustion products. The amount of inhibitor which must be introduced to reduce significantly the combustibility of the polymer is usually extremely large. Thus self-extinguishing compositions based on polyethylene can be obtained only in the presence of at least 20–30 wt.% of the inhibitor.

Additives introduced in the form of mechanical admixtures are sometimes classified as chemically active and inert, although there is no sharp boundary between them. Mineral fillers such as SiO_2, chalk, kaolin, $Al_2O_3.3H_2O$, etc. may be referred to by convention as inert, while active fillers include Sb_2O_3 and alkali metal, barium, zinc, etc. borates and metaborates.

Chloralkanes (with a chlorine content up to 70%) alkyl and aryl phosphates and their halogeno-derivatives, etc. are used as plasticisers which reduce combustibility. In the chemical modification of a polymer carried out to reduce its combustibility halogens and phosphorus are introduced into its structure. A variant of this method involves the modification of the surface layers of the polymer only (halogenation, chlorosulphonation, etc.).

In the development of methods for suppressing the combustion of polymers one usually endeavours to achieve the following aims:

1. The reduction of the heat of combustion of polymeric materials following the introduction of thermodynamically inert additives. Particularly effective additives decompose with a fairly large endothermic heat change within the limits of the condensed phase of the polymer, which lowers the temperature of the surface of the latter and the rate of its combustion.

2. The formation on the polymer surface of a dense carbon residue under the influence of inhibitors, which prevents the supply of heat from the flame to the surface of the polymer and the diffusion of the polymer gasification products to the combustion zone. Readily fusible inhibitors, forming a layer of inert melt on the surface of the polymer, can act similarly.

3. The inhibition by additives (or their reaction products) of the chain oxidation reactions in the flame over the polymer surface.

X. CHEMICAL DEGRADATION AS A METHOD FOR THE MODIFICATION OF THE SURFACES OF POLYMERS

In many cases the operating properties of polymeric articles (for example, fibres and films) are determined by the properties of their surface. Chemical degradation permits a specific modification of the properties of the surfaces of polymers. It is important that the reaction should then involve only those macromolecules which are directly on the surface.

Under real conditions, the modification reaction takes place in a surface layer whose size depends on the ratio of the rate of diffusion of catalysts and reactants to the rate of decomposition of the chemically unstable bonds of the functional groups of the polymer.

The rate of decomposition of chemically unstable polymer bonds is

$$\frac{\partial c_n}{\partial t} = k(c_m^0 - c_n)\, c_{cat} c_{react}, \quad (50)$$

where c_m^0 is the initial concentration of the chemically unstable bonds, c_n the concentration of the bonds which have been ruptured, and c_{cat} and c_{react} are the concentrations in the catalyst and the reactant in the polymer respectively.

The changes in the concentrations of the catalyst and reactant in the polymer are described by the equations

$$\frac{\partial c_{cat}}{\partial t} = D_{cat}\nabla^2 c_{cat} - \sum_i k_i c_{cat} c_i, \quad (51)$$

$$\frac{\partial c_{\text{react}}}{\partial t} = D_{\text{react}}\nabla^2 c_{\text{react}} - k(c_m^0 - c_n)c_{\text{cat}}c_{\text{react}}, \quad (52)$$

where c_i is the concentration of the functional groups in the polymer capable of reacting with the catalyst with a rate constant k_i, D the diffusion coefficient, and ∇^2 the Laplace operator.

In the general case Eqns. (50)–(52) do not have an analytical solution but they can be solved on a computer. The equations are simplified if, for example, the reactant is water (hydrolytic reaction). In the diffusion of catalysts with a low vapour pressure into hydrophobic polymers we then have $D_{H_2O} \gg L_{cat}$ and the concentration of the reactant in the reaction layer is constant and equal to $c^0_{H_2O}$. In the case of catalysts with a high vapour pressure the diffusion of the catalyst and the solvent can be characterised by a single diffusion coefficient, since $D_{H_2O} \simeq D_{cat}$.

The case where the degradation proceeds under steady-state conditions in which the catalyst and reactant concentration gradients in the reaction layer are constant in time is frequently encountered. If the macromolecules decompose at random, the fragments formed on the polymer surface flake off and decompose in solution, i.e. $c^0_m - c_n \simeq c^0_m$. In this case the solution is

$$c_n = k_{\text{eff}}\, c^0_{\text{cat(surf)}} \cdot t \sqrt{\frac{D_{\text{cat}}}{k_{\text{eff}}}} \tanh\left(\frac{L}{2}\sqrt{\frac{k_{\text{eff}}}{D_{\text{cat}}}}\right), \quad (53)$$

where L is the thickness of the reaction layer on the surface of the polymeric article and $c^0_{\text{cat(surf)}}$ the concentration of the catalyst at the polymer–medium interface.

If the rate of decomposition of chemically unstable bonds is much greater than the rate of diffusion,

$$\frac{L}{2}\sqrt{\frac{k_{\text{eff}}}{D_{\text{cat}}}} \gg 1,$$

then

$$c_n = k_{\text{eff(surf)}} c^0_{\text{cat(surf)}} t, \quad (54)$$

where $k_{\text{eff(surf)}} = k_{\text{eff}}\sqrt{D_{\text{cat}}/k_{\text{eff}}}$ and the degradation reaction proceeds virtually on the surface of the polymeric article. This condition holds, for example, in the degradation of poly(ethylene terephthalate) (PETP) in concentrated KOH solutions [112].

The relative change in thickness (l) and mass (m) of the PETP film in concentrated solutions of alkalis is described by the equation

$$\frac{l}{l_0} = \frac{m}{m_0} = \left(1 - \frac{t}{\tau}\right), \quad (55)$$

where $\tau = l_0\rho / k_{\text{eff(surf)}} c^0_{\text{cat(surf)}}$ is the time required for the total decomposition of the polymer and ρ is the density of the polymer.

We shall now consider examples of the employment of the chemical degradation of polymer for the improvement of the properties of their surfaces.

1. The Preparation of Poly(ethylene terephthalate) Films with a Rough Surface

Films with a rough surface are used in modern computers, in radioelectronic, video-recording, and sound recording apparatus, in electrotechnical industry, and in cartography.

According to the generally accepted etching mechanism, a rough surface is formed when the amorphous phase is etched away and the bared crystallites form microrugosities [113]. Rudakova et al. [112] showed for the first time that, in degradative etching on the surface, a roughness arises as a result of the exposure of microdefects (for example, micropores) as the surface layer of the polymer is decomposed. As a result of the wedging pressure, the microdefects then initiate the growth of cracks. The number of micropores is non-uniform with respect to the thickness of the specimen, decreasing with increasing degree of crystallinity. It is to be expected that the surface with the greatest degree of roughness would be obtained in the etching of amorphous polymers.

Fig. 29 illustrates the dependence of the roughness factor Ra on the thickness of the layer λ removed from the surface of PETP films with different degrees of crystallinity. Evidently the maximum value of Ra is observed for amorphous PETP films following the decomposition of a 25–30 μm layer.

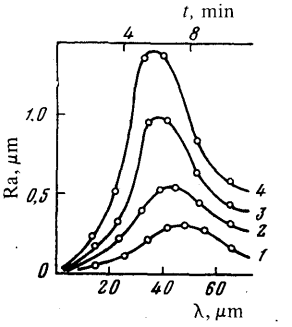
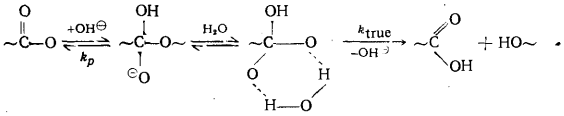


Figure 28. Dependence of the roughness factor Ra for poly(ethylene terephthalate) films treated with 49% KOH (108 °C) on the size of the decomposed layer λ and the degree of crystallinity (%): 1) 58; 2) 40; 3) 30; 4) 5.

Hydrolysis of the ester linkages in PETP proceeds via the mechanism [112]



The variation of k_{eff} with the thermodynamic parameters of the medium is described by the equation

$$K_{\text{eff}} = \frac{k_{\text{true}}\, a_{H_2O}}{1 + K_p/b_0}, \quad (56)$$

where K_p is the equilibrium constant for the addition of a hydroxide ion to the carbonyl carbon atom, b_0 the alkalinity, a parameter proportional to a_{OH^-}, a_{H_2O} the activity of water, and k_{true} the true rate constant.

The overall equation describing the variation of l with time, temperature, and the thermodynamic parameters of the medium is

$$l = l_0 - \frac{A\exp(-E/RT)\, a_{H_2O}\, t}{(1 + K_p/b_0)\rho}. \quad (57)$$

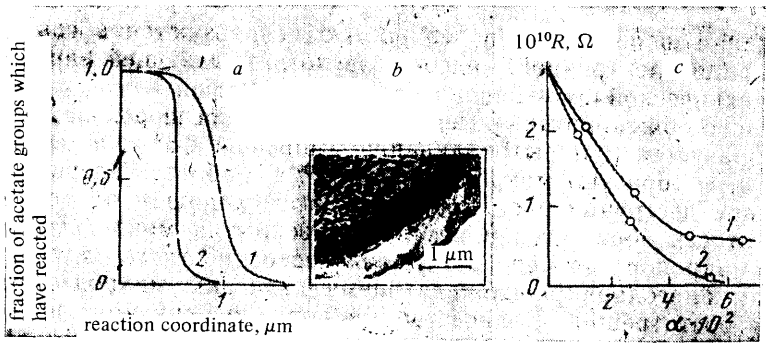


Figure 29. Preparation of diacetate filaments with reduced susceptibility to acquisition of an electrostatic charge: *a*) migration of the reaction front calculated by equations with $t/\tau = 0.1$ (τ is the time corresponding to the end of reaction) in solutions of different alkalis [1) NaOH; 2) $(C_4H_9)_4NOH$]; *b*) photomicrograph of a cross-section of the diacetate filament; *c*) dependence of the resistance of diacetate filaments R on the degree of conversion of the acetate groups in the filament α.

For this form of degradation, the degree of crystallinity of PETP has almost no influence on the kinetic parameters and Eqn. (57) makes it possible to find the optimum conditions for the etching of PETP films.

2. Preparation of Fibres with Reduced Susceptibility to the Acquisition of an Electrostatic Charge

A disadvantage of synthetic and artificial polyester fibres is their high susceptibility to the acquisition of an electrostatic charge. The employment of antistatic agents is frequently undesirable, since many of them can be readily eluted from the polymer and act as irritants to the skin and the mucous membrane of the eye.

Surface degradation is used successfully to reduce the susceptibility of artificial and synthetic fibres to the acquisition of an electrostatic charge. For example, such susceptibility of fabrics can be diminished if the hydrophobic ester groups in the surface layer of cellulose diacetate or triacetate filaments is replaced by the hydrophilic hydroxy-group of the regenerated cellulose. The conditions under which the rate of hydrolysis of the ester linkages is much higher than the rate of diffusion of the alkali into the filaments have been determined[114]. This is achieved (Fig. 29) by (1) using concentrated solutions of strong alkalis, i.e. by increasing k_{eff} for D_{cat} [Eqn. (53)] and (2) by employing alkali with a large bulky cation, for example $(C_4H_9)_4NOH$, i.e. by diminishing D_{cat} for a constant rate of hydrolysis, Both procedures lead to an appreciable reduction of the susceptibility of cellulose to the acquisition of an electrostatic charge.

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Thus, over an extremely short period, the field of the ageing and stabilisation of polymers has become an important branch of the fundamental and applied chemical science, which is concerned with the study of the chemical changes in polymers and polymeric materials and with the development of rational methods for controlling these changes.

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Thermochemical Studies Necessary for the Selection of Key Thermodynamic Quantities

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The present state of experimental studies necessary for calculating key thermodynamic quantities has been reviewed. A list of substances for which experimental measurements of the enthalpies of formation, entropies, etc. are desirable has been proposed. Various problems in the calculation of the standard thermodynamic quantities for solutions have been examined. A list of international recommendations on key thermodynamic quantities has been given. The bibliography contains 50 references.

CONTENTS

I. Introduction 1168
II. Experimental studies of particular interest for the selection of key thermodynamic quantities 1169
III. Appendix 1172

I. INTRODUCTION

Thermodynamic quantities such as the enthalpy and free energy of formation and entropy represent a system of inter-related quantities. Thus the enthalpy of formation of methane depends on the values of the enthalpy of formation of H_2O and CO_2. The free energy, enthalpy of formation, and entropy of a substance are related by the equation $\Delta G = \Delta H - T\Delta S$. Thus with the exception of the standard entropy, the choice of the numerical value of a thermodynamic quantity from published data, or its calculation from experimental measurements, usually cannot be made without certain calculations using various other quantities. The quantities which are most frequently used in these calculations are usually called key thermodynamic quantities.

The quantities usually regarded as key quantities are the values of the enthalpy of formation and entropy at 298.15 K and the enthalpy $H^0_{298} - H^0(0)$ for such substances (basic(as H_2O (liquid, gas), CO_2(gas(, HF (gas), SiO_2 (α-quartz), NH_3 (gas), NH_3 (gas), O_2 (gas), H (gas), B (gas), Cl^- (aq), SO_4^{2-} (aq), Na^+ (aq), UO_2^{2+} (aq), etc.; that is the basic substances are usually elements in their standard states and in the state of free atoms, and also one or two compounds of each element and ions in the state of a standard aqueous solution. This is because these substances appear most frequently in thermochemical cycles and other calculations; the choice of values for these quantities influences the numerical values of the thermodynamic properties of a large number of other substances. Thus the values of the enthalpies of formation of H_2O and CO_2 appear in the calculation of the enthalpies of formation of a vast number of organic compounds, and the values of the thermodynamic properties of simple aqueous ions in the ground state appear in the calculation of the thermodynamic characteristics of solutions of acids, alkalis, salts, undissociated ionic complexes, and many salts in the crystalline state.

The choice of key quantities obviously acquires particular importance in the preparation of fundamental reference books on the thermodynamic properties of substances, summarising accumulated experimental material. The most important principle in the production of these reference works — the internal consistency of the values given — requires recalculation of the results of all experimental studies using the same key quantities. Here it is necessary to take account of the fact that, as shown by the experience of the US National Bureau of Standards[1,2] and the Academy of Sciences of the USSR[3,4], the complete production and publication of these fundamental reference works require about 15 years. Simply as a consequence of the fact that the work on the production of these reference books was begun at different times, the values of the thermodynamic properties given in them are based on different key quantities. When these reference works are used, particularly in the calculation of precise experimental measurements, it is necessary to take account of these differences and to avoid the use of values which are inconsistent with one another.

All the inconvenience and the possibility of misunderstanding and confusion introduced by differences in the values of key quantities are obvious. In order to at least partly eliminate these unsatisfactory features immediately and to remove them completely in the future, the Committee On Data For Science And Technology (CODATA) of the International Council Of Scientific Unions in recent years has been preparing single international recommendations of key thermodynamic quantities. Values have already been chosen for 125 substances, and the preparation of recommendations for several more tens of substances is being completed; some of these quantities have been published[5,6]. A complete summary Table is given in the Appendix at the end of the present review.

One of the aims of the present work is to draw the attention of experimentalists to these international recommendations and to discuss various characteristic features of their use in the calculations. It is necessary that in the future these recommendations become a general basis for calculating the results of experimental measurements and in the production of reference works. It should be borne in mind that the reference books widely used as a source of supplementary thermodynamic quantities[1-4] are based on key quantities which do not coincide with new international recommendations. Thus when the latter are used, it is necessary to introduce appropriate corrections to the data from reference works, which is not always easy.

In view of the situation which has now arisen, where in the literature there is lack of agreement on the choice of key quantities, and reference works on the thermodynamic properties of substances are based on different key quantities (which moreover do not coincide with prepared international recommendations), it is appropriate, in the opinion of the present authors, to make the

following recommendations as practical advice to authors of experimental papers. In those cases where the key quantities recommended by CODATA are sufficient (or almost sufficient) for the recalculation, these should be used. In those cases where the necessary recalculations are complex, and a large number of quantities other than those recommended by CODATA are required, it is preferable to use any one of the above mentioned reference works, since this guarantees that the values included in the calculations are consistent with one another. In any case, it is necessary to indicate in published work the source of the supplementary data used in the calculations (as required by an international resolution on the publication of calorimetric and thermodynamic data[7]). The observation of this and other requirements of the resolution[7] ensures the validity of the publication and makes it possible to estimate the reliability of the measurements made and to recalculate the results using other key quantities.

It is to be hoped that the confused situation discussed above, which has arisen as a result of differences in the values of key thermodynamic quantities used in reference works and in individual publications, will be eliminated in the comparatively near future, since it is planned, about 1980, to begin the preparation of an international reference work on the thermodynamic properties of substances.

II. EXPERIMENTAL STUDIES OF PARTICULAR INTEREST FOR THE SELECTION OF KEY THERMODYNAMIC QUANTITIES

The chief aim of the present work is to attempt to draw the attention of experimentalists to various studies of particular interest from the viewpoint of the values of key thermodynamic quantities (and hence from the viewpoint of the production of the future international reference work). In course of work already rried out on the preparation of reference books and on the choice of key quantities, the available published data for a wide range of substances have been critically analysed. It has been found that the results of measurements for a number of the most important substances are insufficiently accurate or non-existent. At the same time, each year there are published the results of studies of a large number of less important substances, the selection of which is apparently determined by accidental factors. For example, in recent years an extensive cycle of studies on the determination of the thermodynamic properties of many tens of selenates has been carried out. However, the standard enthalpy of formation and entropy of the selenate anion, which are key quantities, have not yet been reliably determined, and the choice of these quantities is based on old and unreliable data. Unfortunately, this is not an isolated example. It would thus be extremely valuable if experimentalists, when planning their work, took account of the need for and importance of studies aimed at determining key thermodynamic quantities. These measurements should naturally be particularly careful and precise, and their publication sufficiently detailed.

Some of the most important experimental measurements which are particularly urgently required are listed below; for each type of measurement, the substances are arranged in order of importance and urgency.

1. Entropies of Crystalline Substances

Measurements of the low-temperature heat capacity and their use to determine the standard entropies and enthalpies of substances in the condensed state are particularly important, since standard entropies are usually determined more accurately than the enthalpies and free energies of formation†, and their use in the calculation of key quantities is almost always preferred to other possible methods. A list of substances for which determination of the standard entropies S^0_{298} is necessary is given below; the temperature ranges (in K) in which the heat capacities of these substances were measured are given in brackets: β-$Be(OH)_2$(crystalline); $MgCl_2$(crystalline) (51–298);[8] $CaCl_2$(crystalline) (51–298);[8] $PbCl_2$(crystalline) (15–206)[9]; PbF_2(crystalline); α-PbO(crystalline, red) (51–298);[10] Hg_2Cl_2(crystalline) (22–99)[11] and (100–273);[12] $HgCl_2$ (crystalline); HgO(crystalline, yellow); SnO_2(crystalline); SnO(crystalline) (69.6–292.5);[13] PuO_2(crystalline) (11–100)[14] and (4–25);[15] SeO_2(crystalline) (53.5–305);[16] α-TeO_2(crystalline); TeO_3(crystalline); α-Sb_2O_3(crystalline, cubic) (65–298);[17] β-Sb_2O_3(crystalline, orthorhombic) (56.2–298)[18] and (65–298);[17] Tl_2O(crystalline); Tl_2O_3 (crystalline); MnO(crystalline) (52–298);[20] Mn_2O_3 (crystalline) (50–298);[20] ReO_2(crystalline); ReO_3(crystalline) (2–100)[21] and (1.4–4.2);[22] Tc_2O_7(crystalline); PdO(crystalline); RuO_4(crystalline); RuO_2(crystalline) (0.54–10);[23] IrO2(crystalline) (0.54–10);[23] OsO_2(crystalline); α-WCl_6(crystalline); $MoCl_6$(crystalline); $Cd(OH)_2$ (crystalline); Ta_2O_5(crystalline) (53.4–294);[24] Au_2O_3 (crystalline).

2. Enthalpies of Formation

The measurement of the standard enthalpies of formation is required particularly urgently for the following substances in the condensed and gaseous states: SrO (crystalline), BaO(crystalline), $SrCl_2$(crystalline), $BaCl_2$ (crystalline), NO(gas), H_2S(gas), NH_4NO_3(crystalline), NH_4NO_2(crystalline), BeO(crystalline), α-$BeCl_2$(crystalline), $MgCl_2$(crystalline), $MgSO_4.6H_2O$(crystalline), AlI_3 (crystalline), $MgSO_4.7H_2O$(crystalline), SnO_2(crystalline), ThF_4(crystalline), $AlCl_3$(crystalline), $FeCl_2.4H_2O$(crystalline), $FeCl_3.6H_2O$(crystalline), TeO_2(crystalline), $TiCl_3$ (crystalline), Tl_2O(crystalline), Na_2WO_4(crystalline), Tl_2O_3(crystalline), V_2O_5(crystalline), $CrCl_3$(crystalline), $CrCl_3.6H_2O$(crystalline), $InCl_3$(crystalline), $GaCl_3$(crystalline), $MoCl_5$(Crystalline), $ScCl_3.6H_2O$(crystalline), $DyCl_3$ (crystalline), $LuCl_3$(crystalline).

For most of these substances, measurements of the enthalpy of the reaction with the corresponding metals present particular difficulties.

The direct measurement of the enthalpy of formation of ions in the standard state (that is in infinitely dilute aqueous solution) is impossible. This quantity is deter-

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† Here it should be borne in mind that the typical error of present-day measurements of the standard entropy (if there are no complicating features) is ~0.1 e.u. In the case of the calculation of the free energy or the equilibrium constant at 298 K, this error corresponds to an error in the enthalpy of the reaction of only 0.03 kcal $mole^{-1}$, which is not reached in all thermochemical measurements.

mined by extrapolating the results of measurements of the enthalpy of reaction, carried out at finite concentrations of the solution, to infinite dilution.

It should be noted that in most cases, including fundamental reference works[2,3], the standard heats of reactions in solutions at infinite dilution are determined by empirical extrapolation of the corresponding experimental data, obtained at definite ionic strengths of the solution I, to $I = 0$. These extrapolations have no rigorous theoretical basis; there are more rigorous methods of extrapolation, based on the electrostatic Debye–Hückel theory. As first shown in 1949,[25] in the determination of the form of the functional dependence of the enthalpies of dilution it is possible to use the equation for the mean-stoichiometric activity coefficients of the electrolytes $\gamma_\pm$ in the third approximation of the Debye–Hückel theory‡:

$$\lg \gamma_\pm = -\frac{|z_+ \cdot z_-| S_T \sqrt{I}}{1 + B\mathring{a}\sqrt{I}} + cI + bI^2 + \ldots, \quad (1)$$

where $S_T = 1.8246 \times 10^6 d^{0.5}/(DT)^{1.5}$; $B = 50.294 \times 10^8 d^{0.5}(DT)^{-0.5}$; d is the density of water; D the dielectric constant of water; T the temperature, K; z_i the charge of the ith ion; $I = \frac{1}{2}\Sigma m_i z_i^2$ is the ionic strength of the solution; $\mathring{a}$ the "ionic parameter"; and c and b empirical coefficients.

Using the familiar relationships

$$\bar{L}_2 = -\nu RT^2 \left(\frac{\partial \ln \gamma_\pm}{\partial T}\right)_{p,I}, \quad (2)$$

$$\bar{L}_2 = \varphi_H + m\frac{\partial \varphi_H}{\partial m} \quad (3)$$

and Eqn. (1), Owen and Brinkley[25] obtained in general form the dependence of the heat of dilution of electrolytes on the ionic strength of the solutions:

$$\varphi_H = \nu|z_+ \cdot z_-|\varphi_H\ (\text{D–H}) + c_H I + b_H I^2 + \ldots, \quad (4)$$

where $\nu|z_+ \cdot z_-|\varphi_H$(D–H) is the electrostatic contribution to the heat of dilution according to the Debye–Hückel theory, and c_H and b_H are empirical coefficients.

By solving Eqns. (1)–(3) simultaneously, Khodakovskii and Dorobeeva[26], independently of Owen and Brinkley, obtained an expression for φ_H(D–H):

$$\varphi_H\ (\text{D–H}) = \frac{S_H}{B\mathring{a}} J_1 + \frac{W_H}{(B\mathring{a})^2} J_2, \quad (5)$$

where

$$J_1 = 1 - \frac{2}{B\mathring{a}\sqrt{I}} + \frac{2\ln(1 + B\mathring{a}\sqrt{I})}{(B\mathring{a})^2 I}, \quad (6)$$

$$J_2 = 1 - \frac{4}{B\mathring{a}\sqrt{I}} + \frac{2}{(B\mathring{a})^2 I}\left[\frac{1}{1 + B\mathring{a}\sqrt{I}} + 3\ln(1 + B\mathring{a}\sqrt{I}) - 1\right], \quad (7)$$

and the coefficients S_H and W_H are functions of only temperature and pressure, and their numerical values are given in Ref. 26. The same equations (5)–(7) can be obtained by substituting in the expression for φ_H(D–H) obtained in Ref. 25 the symbols used in Ref. 26, and carrying out the appropriate mathematical transformations.

‡ Only the basic scheme of the calculation is given below. More detailed descriptions can be found in Refs. 25 and 26.

It may therefore be assumed that the analytical form of the relationship (5) has been fairly reliably established.

Since the form of the equation for the dependence of the activity coefficients of individual ions on the ionic strength of the solution is similar to that of Eqn. (1):

$$\lg \gamma_i = -\frac{z_i^2 S_T \sqrt{I}}{1 + B\mathring{a}\sqrt{I}} + cI + bI^2 + \ldots, \quad (8)$$

it is possible, using the approach proposed by Vasil'ev[29], to obtain refined equations for calculating the standard enthalpy change (ΔH°) for any reaction involving ions:

$$\Delta H_I - \Delta z^2 \varphi_H\ (\text{D–H}) = \Delta H^0 + \Delta c_{H,I} + \Delta b_{H,I}^2 + \ldots, \quad (9)$$

where ΔH_I is the enthalpy change of the reaction for an ionic strength of the solution equal to I; Δz^2 the algebraic sum of squares of the charges of the ions taking part in the reaction (for example, for the reaction $CuCl_2 = Cu^{2+} + 2Cl^-$ we have $\Delta z^2 = 4 + 1 + 1 = 6$).

The applicability of Eqn. (9) in the determination of the standard heats of reactions from data for solutions having a high ionic strength (as far as $I = 3$–5) has been demonstrated[26–28]. The use of Eqn. (9) is particularly important in those cases where, from the conditions of the experiment, the calorimetric study of the reaction can be carried out only at high ionic strengths of the solutions, for example for reactions involving multiply-charged cations which are readily hydrolysed in weakly acidic solutions.

Table 1. Comparison of the standard enthalpies of various reactions, calculated using Vasil'ev's equation[29] and Eqn. (9).

Reaction	Δz^2	ΔH^0_{298}, kcal mole^{-1}		Refs.
		from Vasil'ev's Eqn.(29)	from Eqn.(9)	
$Co(cryst.) + H_2O_2(soln.) + 2H^+(soln.) = Co^{2+}(soln.) + 2H_2O(liq.)$	2	−104.07±0.15	−104.13±0.15	36
$Pb(cryst.) + H_2O_2(soln.) + 2H^+(soln.) = Pb^{2+}(soln.) + 2H_2O(liq.)$	2	−90.75±0.20	−90.80±0.20	30
$PbO(cryst., liq.) + 2H^+(soln.) = Pb^{2+}(soln.) + H_2O(liq.)$	2	−15.94±0.07	−15.98±0.07	30
$Fe(cryst.) + \frac{3}{2}H_2O_2(soln.) + 3H^+(soln.) = Fe^{3+}(soln.) + 3H_2O$	6	−147.25±0.15	−147.63±0.15	33
$SnCl_2(cryst.) = Sn^{2+}(soln.) + 2Cl^-(soln.)$	6	−3.22±0.30	−3.58±0.15	31
$SnCl_2.2H_2O(cryst.) = Sn^{2+}(soln.) + 2Cl^-(soln.) + 2H_2O(liq.)$	6	1.03±0.19	0.77±0.07	31
$Bi(cryst.) + \frac{3}{2}H_2O_2(soln.) + 3H^+(soln.) = Bi^{3+}(soln.) + 3H_2O(liq.)$	6	−117.7±1.2	−117.97±0.54	32
$Bi_2O_3(cryst.) + 3H^+(soln.) = Bi^{3+}(soln.) + \frac{3}{2}H_2O(liq.)$	6	−30.45±0.16	−29.86±0.15	32
$ZrCl_4(cryst.) = Zr^{4+}(soln.) + 4Cl^-(soln.)$	20	−70.64±0.29	−71.01±0.60	34
$ZrBr_4(cryst.) = Zr^{4+}(soln.) + 4Br^-(soln.)$	20	−73.39±0.15	−73.48±0.20	34
$HfCl_4(cryst.) = Hf^{4+}(soln.) + 4Cl^-(soln.)$	20	−80.14±0.31	−79.30±0.35	35

It should be noted that in spite of the fact that in the works cited[26,27], attention was drawn to the inaccuracy of the determination of the form of the functional dependence of φ_H(D–H) on the ionic strength of the solutions in Ref. 29, the equation derived in Ref. 29 is still often used (see for example Refs. 33–35) to calculate the standard enthalpies of reactions. Table 1 clearly shows that if the value of Δz^2 is large, the difference in the values of the standard heats of reactions obtained by different extrapolation methods may be considerable, and may exceed the error of the experimental measurements.

The most complex problem in the determination of the standard enthalpies of formation of simple ions which are key quantities is the measurement of the standard enthalpies of formation of such readily hydrolysed cations as Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Fe^{3+}, Cr^{3+}, Mn^{3+}, U^{4+}, Th^{4+}, Pu^{4+}, Sn^{4+}, Ge^{4+}, Zr^{4+}, Hf^{4+} and the anions SO_3^{2-}, $S_2O_3^{2-}$, SeO_3^{2-}, SeO_4^{2-}, TeO_3^{2-}, $Te(OH)_6^{2-}$, S^{2-}, Se^{2-}, Te^{2-}, etc. The standard enthalpies of formation of many of these ions can be determined by measuring the enthalpies of solution of the chlorides of the corresponding elements or their oxides in solutions of perchloric acid or alkali at concentrations of the latter which are sufficient for the practically complete suppression of hydrolysis. At the same time, quantitative allowance for the influence of hydrolysis processes also requires calorimetric measurements of the enthalpies of hydrolysis over a wide range of ionic strengths of the solutions.

3. Standard Entropies of Ions in Aqueous Solution

The most reliable values of the standard entropies for many simple cations and anions in aqueous solution in most cases are obtained from the value of ΔS°_{298} for the solution of the corresponding anhydrous salts or crystalline hydrates in water, in equilibrium with their saturated solutions:

$$K_m^{n+}A_n^{m-} \cdot xH_2O(\text{cryst.}) = mK^{n+}(\text{soln., standard state}) + nA^{m-}(\text{soln., standard state}) + xH_2O(\text{liq.}), \quad (10)$$

and also from the values of the standard entropy of the soluble salt, the entropy of the anion (or cation) and the entropy of H_2O(liquid) (in the case of crystalline hydrates). The values of ΔS°_{298} in turn is calculated from the values of ΔH°_{298} and ΔG°_{298} for reaction (10). For readily soluble salts, the reliable determination of the value of ΔG°_{298} is possible when there are experimental data on the mean-stoichiometric activity coefficients of the solutions $K_mA_n(\gamma\pm)$ and the activity of water in the case of crystal hydrates, up to the saturation concentration (m_{sat}). Since these calculations usually combine data obtained in different laboratories in methodologically different studies, generally not undertaken to solve the problem being considered in the calculations, the literature in many cases contains only some of the necessary data. Salts can be divided into three large groups, depending on the completeness of the available thermodynamic information.

The first group consists of salts for which it is sufficient to determine only one property in order to make possible the accurate calculation of the entropy of the cation (or anion). Thus for a number of salts there are reliable values of ΔS°_{298} for their solution (ΔG°_{298} and ΔH°_{298} for reaction (10) are known), but the calculation of the entropy of the ions cannot be carried out until sufficiently accurate values have been determined for the standard entropies of the corresponding crystalline substances. Accurate values of the latter can be obtained from measurements of the heat capacity in the temperature range 5–300 K. A list of these salts is given below; the temperature ranges (K) in which the heat capacities were measured are given in brackets.

β-$Be(OH)_2$, $MgSO_4\cdot7H_2O$, $Mg(ClO_4)_2\cdot6H_2O$, $Mg(NO_3)_2\cdot6H_2O$ (295—305) [37], $CaCl_2\cdot6H_2O$, $CaSO_4\cdot2H_2O$ (50—298) [39], $Ca(ClO_4)_2\cdot6H_2O$, α-$Ca(NO_3)_2\cdot4H_2O$ (40—300) [38] and (295—305) [37], $SrCl_2\cdot6H_2O$, $Sr(NO_3)_2\cdot4H_2O$, $SrSO_4$ $SrCO_3$(50—298) [39], $Ba(OH)_2\cdot8H_2O$, $Ba(ClO_4)_2\cdot3H_2O$, $Ni(ClO_4)_2\cdot6H_2O$, $Co(ClO_4)_2\cdot6H_2O$, $Mn(ClO_4)_2\cdot6H_2O$, $Mn(NO_3)_2\cdot6H_2O$, $Cu(ClO_4)_2\cdot6H_2O$, ZnI_2, $Zn(ClO_4)_2\cdot6H_2O$, $Zn(NO_3)_2\cdot6H_2O$, $CdCl_2\cdot2{,}5H_2O$, $CdBr_2\cdot4H_2O$, $Cd(NO_3)_2\cdot4H_2O$(160—320) [38], $Cd(ClO_4)_2\cdot6H_2O$, $NaClO_3$, $NaClO_4\cdot H_2O$, $NaBO_3$, $NaSCN\cdot2H_2O$, $Na_2CrO_4\cdot4H_2O$, $NaB(OH)_4\cdot2H_2O$, $NaBF_4$, $Na_3PO_4\cdot12H_2O$, K_2CrO_4 (60—300) [41], $K_2Cr_2O_7$ (80—300) [41, 42], KIO_4, $CsNO_3$, $CsBrO_3$, $RbBrO_3$, $RbNO_3$, $AgBrO_3$, Ag_2SeO_3, Ag_2SeO_4, Ag_2MoO_4, Ag_2WO_4, $ScCl_3\cdot6H_2O$, $UO_2SO_4\cdot2.5H_2O$, $UF_4\cdot2{,}5H_2O$, $ThF_4\cdot2.5H_2O$.

Salts for which only measurement of the enthalpy of reaction (10) is required: $AlCl_3.6H_2O$, $NH_4Al(SO_4)_2.12H_2O$, $NH_4Cr(SO_4)_2.12H_2O$, $(NH_4)_2SnCl_6$, K_2SnCl_6.

Salts for which only measurements of $\gamma\pm$ and a_{H_2O} for m_{sat} are required: $FeSO_4.7H_2O$, Cs_2CrO_4, $SnCl_2.2H_2O$, $(NH_4)_2SiF_6$, Na_2SiF_6, $NaHCOO.2H_2O$.

In the determination of the entropies of crystalline hydrates it is necessary to take account of the fact that some of them have a residual entropy at 0 K. To determine this it is necessary to know the entropy of the anhydrous salt (or crystalline hydrates containing a smaller number of water molecules) and the enthalpy changes in the dehydration. The latter can be calculated if the dissociation pressures of the crystalline hydrates and the enthalpies of solution of the anhydrous salts and the crystalline hydrates in water to give solutions of the salt having the same concentration are known. Examples of these calculations can be found in papers dealing with the determination of the standard entropies of $Na_2SO_4.10H_2O$,[43] $Na_2CO_3.10H_2O$,[44] $Na_2HPO_4.12H_2O$,[45] $ZnF_2.4H_2O$,[46] $ZnSO_4.7H_2O$,[47] etc.

The second group consists of salts for which two types of experimental study are required, namely:

a) ΔH°_{298} for reaction (10); $\gamma\pm$ and a_{H_2O} for m_{sat}—for Cs_2MoO_4, SnI_2, $SnSO_4$, NaN_3.

b) ΔS°_{298}; $\gamma\pm$ and a_{H_2O} for m_{sat}—for K_2SeO_3, K_2SeO_4, $Na_2SeO_3.5H_2O$, $Na_2TeO_3.5H_2O$, Li_2TeO_3, $CaSeO_4.2H_2O$, $NaVO_3.2H_2O$, $NpO_2(NO_3)_2.6H_2O$, $PuCl_3.6H_2O$, K_2PdCl_4, K_2PtCl_4.

c) ΔH°_{298} for reaction (10); S°_{298}—for $Cr(NO_3)_3.9H_2O$, $Cr_2(SO_4)_3.18H_2O$, $K_3PO_4.7H_2O$, $K_2HPO_4.3H_2O$, $K_4P_2O_7.3.5H_2O$, $Na_2SO_4.7H_2O$, α-$NaH_2AsO_4.H_2O$, $K_3AsO_4.7H_2O$, $K_2HAsO_4.3H_2O$, $Na_3AsO_4.8H_2O$, $NaCN.2H_2O$, $Na_2SiO_3.9H_2O$, $Na_2GeO_3.7H_2O$.

Finally, for salts of the third group there are no thermodynamic data making it possible to characterise reaction (10), except the concentration of the saturated solution, and for these, the measurement of all three properties is required: $NaIO_4.3H_2O$, $H_2TeO_4.2H_2O$, $U(SO_4)_2.8H_2O$, $Th(SO_4)_2.9H_2O$, $Zr(SO_4)_2.4H_2O$, $CrSO_4.7H_2O$, $Sc(NO_3)_3.4H_2O$, $Na_2H_2PO_3.2{,}5H_2O$, KVO_3, α-$Na_3VO_4.12H_2O$, $UO_2CrO_4.5.5H_2O$, $Bi(NO_3)_3.5H_2O$, $Hg(ClO_4)_2.6H_2O$, $Na_2.MoO_4.2H_2O$, $Na_2WO_4.2H_2O$.

In the field of high-temperature studies, it is desirable to obtain more accurate values for the enthalpies of sublimation of a number of elements (for example, Ge, B, Zr, U, Re, Tc, Si, Be, Al, and the actinides), to study the energies of dissociation and enthalpies of formation of gaseous As_4, As_2, Sb_4, Sb_2, Tc_2, Se_2, N_2, and O_2, and to study the spectra of atoms with incomplete electron levels (transition metals, lanthanides, actinides) to determine the types of ground electronic states and the energies of the low electronic states.

The thermodynamic studies proposed above, which should lead to a significant increase in the accuracy of key quantities, is of course to some extent subjective and incomplete, and may be extended considerably. The present authors hope that experimentalists in the field of thermodynamics will consider precise studies of the above substances.

III. APPENDIX

Key Thermodynamic Quantities Recommended by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions§

Substance	State	ΔH^0_{298}, kJ mole^{-1}	S^0_{298}, J K^{-1} mole^{-1}	$H^0_{298}-H^0(0)$, kJ mole^{-1}
O	gas	249.17±0.10	160.946±0.020	6.728±0.003
O_2	gas	0	205.037±0.033	8.682±0.004
H	gas	217.997±0.006	114.604±0.015	6.197±0.002
H^+	aq	0	0	—
H_2	gas	0	130.570±0.033	8.468±0.003
OH^-	aq	−230.025±0.045	−10.71±0.20	—
H_2O	liquid	−285.830±0.042	69.950±0.080	13.293±0.020
H_2O	gas	−241.814±0.042	188.724±0.040	9.908±0.008
He	gas	0	126.039±0.012	6.197±0.002
Ne	gas	0	146.214±0.016	6.197±0.002
Ar	gas	0	154.732±0.020	6.197±0.002
Kr	gas	0	163.971±0.020	6.197±0.002
Xe	gas	0	169.573±0.020	6.197±0.002
F	gas	79.39±0.30	158.640±0.020	6.518±0.004
F^-	aq	−333.35±0.65	−13.18±0.54	—
F_2	gas	0	202.685±0.040	8.825±0.004
HF	gas	−273.30±0.70	173.665±0.035	8.599±0.004
Cl	gas	121.302±0.008	165.076±0.020	6.272±0.003
Cl^-	aq	−167.080±0.088	56.73±0.16	—
Cl_2	gas	0	222.965±0.040	9.180±0.008
HCl	gas	−92.31±0.13	186.786±0.033	8.640±0.004
Br	gas	111.86±0.12	174.904±0.020	6.197±0.020
Br	aq	−121.50±0.15	82.84±0.20	—
Br_2	liquid	0	152.210±0.040	24.52±0.13
Br_2	gas	30.91±0.11	245.350±0.054	9.724±0.012
HBr	gas	−36.38±0.17	198.585±0.033	8.648±0.004
I	gas	106.762±0.040	180.673±0.020	6.197±0.002
I^-	aq	−56.90±0.84	106.70±0.20	—
I_2	crystalline	0	116.139±0.080	13.196±0.040
I_2	gas	62.421±0.080	260.567±0.063	10.117±0.021
HI	gas	26.36±0.80	206.480±0.040	8.657±0.006
S	crystalline, orthorhombic	0	32.054±0.050	4.412±0.060
S	gas	276.98±0.25	167.715±0.035	6.657±0.004
S_2	gas	128.49±0.30	228.055±0.050	9.131±0.008
SO_2	gas	−296.81±0.20	248.11±0.06	10.548±0.013
SO_4^{2-}	aq	−909.60±0.40	18.83±0.50	—
N	gas	472.68±0.40	153.189±0.020	6.197±0.002
N_2	gas	0	191.502±0.025	8.669±0.003
NO_3^-	aq	—	146.94±0.85	—
NH_3	gas	−45.94±0.35	192.67±0.08	10.046±0.008
NH_4^+	aq	−133.26±0.25	111.17±0.75	—
P	crystalline, white	0	41.09±0.25	5.360±0.015
P	gas	316.5±1.0	163.085±0.020	6.197±0.002
P_2	gas	144.0±2.0	218.01±0.04	8.903±0.008
P_4	gas	58.9±0.3	279.9±0.5	14.10±0.24
C	crystalline, graphite	0	5.74±0.12	1.050±0.020
C	gas	716.67±0.44	157.988±0.020	6.535±0.006
CO	gas	−110.53±0.17	197.556±0.032	8.673±0.008
CO_2	gas	−393.51±0.13	213.677±0.040	9.364±0.008
Si	crystalline	0	18.81±0.08	3.217±0.008
Si	gas	450±8	167.870±0.035	7.550±0.004
SiO_2	α-quartz	−910.7±1.0	41.46±0.20	6.916±0.020
SiF_4	gas	−1614.95±0.85	282.65±0.40	15.38±0.05
Ge	crystalline, cubic	0	31.09±0.13	4.636±0.015
GeO_2	crystalline, tetragonal	−580.2±1.2	39.71±0.15	7.230±0.020
GeF_4	gas	−1190.15±0.50	301.8±1.0	17.30±0.08
Sn	crystalline, white	0	51.18±0.08	6.323±0.008
Sn	gas	301.2±1.7	168.380±0.020	6.215±0.002
Sn^{2+}	aq	−8.9±0.8	−15.8±4.0	—
SnO	crystalline	−285.93±0.70	57.17±0.30	8.736±0.022
SnO_2	crystalline	−580.78±0.40	52.3±1.2	8.76±0.08
Pb	crystalline	0	64.80±0.30	6.870±0.020
Pb	gas	195.20±0.80	175.270±0.020	6.197±0.002
Pb^{2+}	aq	0.92±0.25	17.7±0.8	—
$PbSO_4$	crystalline	−919.94±0.90	148.49±0.40	20.050±0.040
B	crystalline	0	5.90±0.08	1.222±0.008
B	gas	560±12	153.325±0.035	6.315±0.004
B_2O_3	crystalline	−1273.5±1.4	53.97±0.30	9.301±0.040
BF_3	gas	−1135.95±0.80	254.31±0.10	11.650±0.020
Al	crystalline	0	28.35±0.08	4.565±0.010
Al	gas	329.7±4.0	164.440±0.030	6.919±0.004
Al_2O_3	α-corundum	−1675.7±1.3	50.92±0.10	10.016±0.020
AlF_3	crystalline	−1510.4±1.3	66.5±0.4	11.62±0.04
Zn	crystalline	0	41.63±0.13	5.657±0.020
Zn	gas	130.42±0.20	160.875±0.025	6.197±0.002

Key Thermodynamic Quantities (continued)

Substance	State	ΔH^0_{298}, kJ mole^{-1}	S^0_{298}, J K^{-1} mole^{-1}	$H^0_{298}-H^0(0)$, kJ mole^{-1}
Zn^{2+}	aq	−153.39±0.20	−109.6±0.7	—
ZnO	crystalline	−350.46±0.27	43.64±0.40	6.933±0.040
Cd	crystalline	0	51.80±0.15	6.247±0.004
Cd^{2+}	aq	−75.88±0.60	−72.8±1.2	—
CdO	crystalline	−258.1±0.8	54.8±1.7	8.41±0.08
$CdSO_4 \cdot {}^8/_3\ H_2O$	crystalline, monoclinic	−1729.55±0.80	229.66±0.40	35.56±0.04
Hg	liquid	0	75.90±0.12	9.342±0.008
Hg	gas	61.38±0.04	174.860±0.020	6.197±0.002
Hg^{2+}	aq	170.16±0.20	−36.32±0.80	—
Hg_2^{2+}	aq	166.82±0.20	65.52±0.80	—
HgO	crystalline, red	−90.83±0.12	70.25±0.30	9.117±0.025
Hg_2Cl_2	crystalline	−265.45±0.30	191.6±1.5	23.35±0.20
Hg_2SO_4	crystalline	−743.41±0.50	200.71±0.20	26.070±0.030
Cu	gas	0	33.15±0.08	5.004±0.008
Cu	aq	337.6±1.2	166.285±0.025	6.197±0.002
Cu^{2+}	crystalline	65.69±0.80	−97.1±1.2	—
$CuSO_4$	crystalline	−771.1±1.2	109.2±0.4	16.86±0.08
Ag	gas	0	42.55±0.21	5.745±0.020
Ag	aq	284.9±0.8	172.883±0.025	6.197±0.002
Ag^+	crystalline	105.750±0.085	73.38±0.40	—
AgCl	crystalline	−127.070±0.085	96.23±0.20	12.033±0.040
Th	gas	0	53.39±0.40	6.510±0.020
Th	crystalline	598±6	190.06±0.04	6.197±0.002
ThO_2	crystalline	−1226.4±3.5	65.23±0.20	10.560±0.020
U	crystalline	0	50.20±0.20	6.364±0.020
UO_2	aq	−1085.0±1.0	77.03±0.20	11.280±0.020
UO_2^{2+}	crystalline (γ)	−1019.2±2.5	−98.3±4.0	—
UO_3	crystalline	−1223.8±2.0	96.11±0.40	14.585±0.080
U_3O_8	crystalline	−3574.8±2.5	282.55±0.50	42.74±0.10
Be	gas	0	9.50±0.08	1.950±0.020
Be	crystalline	324±5	136.165±0.020	6.197±0.002
BeO	crystalline	−609.4±2.5	13.77±0.04	2.837±0.008
Mg	gas	0	32.68±0.10	5.000±0.030
Mg	crystalline	147.10±0.80	148.535±0.020	6.197±0.002
MgO	crystalline	−601.5±0.3	26.95±0.15	5.160±0.020
MgF_2	gas	−1124.2±1.2	57.2±0.4	9.92±0.06
Ca	aq	0	41.6±0.4	5.73±0.04
Ca	crystalline	177.8±0.8	154.775±0.020	6.197±0.002
Ca^{2+}	crystalline	−543.10±0.80	−56.4±0.4	—
CaO	aq	−635.09±0.90	38.1±0.4	6.75±0.06
Li	crystalline	0	29.12±0.20	4.632±0.040
Li^+	aq	−278.455±0.090	11.30±0.35	—
Na	crystalline	0	51.30±0.20	6.460±0.020
Na^+	aq	−240.300±0.065	58.41±0.20	—
K	crystalline	0	64.68±0.20	7.088±0.020
K^+	aq	−252.17±0.10	101.04±0.25	—
Rb	crystalline	0	76.78±0.30	7.489±0.020
Rb^+	aq	−251.12±0.13	120.46±0.40	—
Cs	crystalline	0	85.23±0.40	7.711±0.020
Cs^+	aq	−258.04±0.13	132.84±0.40	—

§ The recommended values were prepared by the International Task Group of CODATA for Key Thermodynamic Quantities: J. B. Cox (Present President of the Group), J. Drowart, L. V. Gurvich, V. A. Medvedev, J. B. Pedley, S. Sunner, D. D. Wagman, L. G. Hepler, and W. H. Evans. From the Soviet Union, the following also took part in this work: G. A. Bergman, V. P. Vasil'ev, A. F. Vorob'ev, G. L. Gal'chenko, V. P. Kolesov, I. L. Khodakovskii, and V. S. Yungman. The Table includes material published in CODATA Bullentins (see Ref. 48), including Bulletins[49,50] published after the Seventh All Union Conference. In addition to the above CODATA Bulletins and other publications[5,6], more detailed and complete information on key thermodynamic quantities, including commentaries, bibliographies, atomic weights, energy units, etc. will be published in a special information bulletin being prepared by the State Standard Reference Data Service of Gosstandardt SSSR (USSR State Standards).

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Advances in the Thermodynamics of Organic Compounds in the USSR

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The results of the determination of the thermochemical parameters of organic and organometallic compounds as well as studies on the thermodynamic criteria of the occurrence of polymerisation and polycondensation processes and reactions involving products of petrochemical synthesis, carried out in the USSR during 1971-1975, are described.
The bibliography includes 114 references.

CONTENTS

I.	Introduction	1174
II.	Enthalpies of combustion and formation	1174
III.	The low-temperature heat capacity and thermodynamic functions	1177
IV.	Thermodynamics of polymerisation and polycondensation processes	1179
V.	Thermodynamics of reactions of products of petrochemical synthesis and other processes	1182
VI.	Liquid-vapour equilibria involving pure substances	1182

I. INTRODUCTION

In order to lay the scientific foundations of the technology for the synthesis of new substances with the aim of obtaining materials having specified properties, it is necessary to determine optimum conditions, in the thermodynamic sense, for the new processes, i.e. conditions ensuring the optimum yield of products. It is therefore necessary to determine the enthalpies of formation and the entropies of many new substances and to calculate the Gibbs free energies of new processes as a function of temperature, pressure, and the reactant concentrations. Experimentally, this is mainly associated with the development of calorimetric research into the enthalpies of reaction and the temperature dependence of the heat capacities of substances. It is also extremely important to investigate phase equilibria involving new pure compounds and multicomponent systems of technological importance.

Since it is impossible to reflect the specific advances in all the fields indicated above in a single review, mainly studies on several fundamental subjects will be considered: studies on the enthalpies of combustion and formation of organic and organometallic compounds; measurements of their low-temperature heat capacities and thermodynamic functions; studies on the thermodynamics of a number of processes.

These investigations were carried out in the laboratories of thermodynamics and thermochemistry of Moscow, Gorky, and Belorussian State Universities, the Institute of Chemical Physics of the USSR Academy of Sciences, the State Institute of Applied Chemistry, the Mendeleev Moscow Institute of Chemical Engineering, the Kuibyshev Polytechnic Institute, and a number of laboratories of higher educational establishments and academic and industrial research institutes.

During the period indicated above, our laboratories have successfully applied new precision USSR produced apparatus—a bomb calorimeter rotating simultaneously about two mutually perpendicular axes, constructed by Kolesov[1], and a calorimeter with a microfurnace within the bomb, constructed by Gal'chenko[2] (Moscow State University); apparatus for the measurement of heat capacities from 4 K based on a special cryostat at the Physicotechnical Low-Temperature Institute of the Academy of Sciences of Ukrainian SSR[3] and a universal thermophysical apparatus of the VNIIFTRI (All-Union Institute of Physicotechnical and Radiotechnical Measurements)[4]; a differential automatic calorimeter (DAK-1) for the determination of the enthalpies of mixing of the SKB [synthetic rubber bureau (?)] of the USSR Academy of Sciences[5], and other apparatus. In particular automation designed to maintain precise adiabatic conditions in the measurements of the heat capacities in the above apparatus and the treatment of the results on a computer made it possible to increase significantly the productivity of the experiments.

There have been significant methodological advances. These involve the improvement of the technique of the combustion of gaseous and condensed of organic and fluoro- and chlorofluoro-compounds (Kolesov, Moscow State University[6]), the development of methods for the determination of the enthalpies of combustion of carbaboranes based on an explosive process (Gal'chenko, Moscow State University[7]), and the development of a novel technique for the determination of enthalpies of sublimation in a Calvet microcalorimeter[8] in relation to organoboron compounds (Moscow State University and the Institute of Chemical Physics of the USSR Academy of Sciences), and others.

In most of the studies adequate attention has been devoted to the purification and monitoring of the purity of substances and the estimation of errors of measurements. The purity in the relevant instances was not less than 99.9%; the error in the measurement of the enthalpies of combustion was 0.01-0.05%, depending on the nature of the substances, and that in the heat capacities was 0.2 to 0.5%, depending on the temperature range.

II. ENTHALPIES OF COMBUSTION AND FORMATION†

Mainly traditional studies on organohalogen and organoboron compounds have been continued at the Luginin Thermochemical Laboratory (Moscow State University). Table 1 presents the results of the determination of the enthalpies of combustion ($\Delta H°_c$) and formation ($\Delta H°_f$) of 19 organic chlorofluoro-compounds studied by Kolesov

† Throughout the text below, 1 cal = 4.1840 J, (g) or g denotes a gas, (liq) or liq denotes a liquid, (c) or c denotes a crystal, soln denotes a solution, v-e denotes the viscoelastic state, and v denotes the vitreous state. The superscript 0 to the thermodynamic functions indicates a standard state of 101.325 kPa.

and coworkers[6,9-14] (chlorofluoroalkanes and oxygen-containing organofluorine compounds — derivatives of alcohols, acids, ethers, and esters). The experimental data were used to determine the enthalpies of formation of fluoroethylenes, to select reference quantities for the calculation of the $\Delta H°_f$ of fluoro- and chlorofluoroalkanes by the method of group contributions, and to establish for oxygen compounds in what cases and to what extent the mutual influence of the electrophilic atoms and groups is manifested in the energy of formation of molecules. In 1976 Kolesov wrote a critical review on the thermochemistry of halogenomethanes[14]. Using his own and literature experimental data, he selected 17 reference values of $\Delta H°_f$ and calculated by the method of group contributions the enthalpies of formation of all the 70 halogenomethanes. Many of the halogenoalkanes are used in industry and their enthalpies of formation are necessary for technological calculations.

Table 1. The enthalpies of combustion and formation of organic chlorofluoro-compounds at 298.15 K.

Compound	$-\Delta H°_c$*, kcal mole^{-1}	$-\Delta H°_f$ (liq; c), kcal mole^{-1}	$-\Delta H°_f$ (g), kcal mole^{-1}	Refs.
$CH_2 = CHF$(g)	300.20±0.4	—	32.5	9
CF_3CHFCl(g)	298.22±0.6	—	74.1	11
$CF_3CH_2CH_2Cl$ (liq)	359.52±0.22	191.04±0.22	184.03	9
$CF_3CH_2CHCl_2$ (liq)	324.34±0.27	197.89±0.27	189.75	6
$CF_3CH_2CCl_3$ (liq)	295.01±0.22	198.53±0.22	189.83	9
$CF_3CH_2CF_3$ (g)	271.0±1.7	—	331.5	9
$CF_3CH_2CF_2Cl$ (liq)	288.27±0.17	278.36±0.18	271.94	11
CF_3CH_2OH (liq)	196.06±0.19	220.55±0.19	210.21	9
$CF_3CF_2CH_2OH$ (liq)	274.79±0.68	319.90±0.68	308.99	9
$CF_3(CF_2)_2CH_2OH$ (liq)	323.46±0.16	263.27±0.16	253.13	9
$CF_3CH_2CH_2OH$ (liq)	349.57±0.38	229.41±0.39	217.81	9
$CHF_2CF_2CH_2OH$ (liq)	323.46±0.16	263.27±0.16	251.28	9
$(CF_2)_4(CH_2OH)_2$ (c)	592.0±1.1	513.3	492.0	12
CF_3COOH (liq)	94.9±0.4	253,4±0.4	244.2	6,13
$CF_3CF_2COOCH_3$ (liq)	342.88±0.41	345.84±0.42	337.54	10
$(CF_2)_3C(COOCH_3)_2$ (liq)	647.0±1.0	468.4	459.1	10
$(CF_3CH_2CH_2)_2O$ (liq)	700.97±0.24	388.65±0.25	378.85	10
$(C_4F_9)_2O$ (liq)	561.78±0.73	946.8±0.7	937.1	13
$(C_5F_{11})_2O$ (liq)	721.5±3.6	1143.2	1131.9	13

* The final state for $\Delta H°_c$ was as follows: CO_2(g), H_2O.(liq), HCl(soln), HF(soln), and N_2(g).

Table 2 lists the enthalpies of combustion and formation of a number of representatives of 15 organoboron compounds of different classes studied by Gal'chenko and coworkers[2,7,8,15-17] [the carbaboranes $B_{10}C_2H_{12}$ and their derivatives, whose molecules contain a closed skeleton (nucleus) of boron and carbon atoms; acyclic aminoboranes; dialkyl-(γ-aminopropyl)boranes — boron–nitrogen inner complexes in which ring closure takes place via the N–B bond; azaborolidines and oxaborolanes — compounds with a five-membered ring incorporating B and N or B and O atoms respectively]. Apart from their independent importance, the results of these studies, continuing the many years of research by Gal'chenko into the thermochemistry of boron compounds, made it possible to discover and explain many regularities in the properties of these substances. In particular, it is of interest that the enthalpies of isomerisation of unsubstituted carbaboranes proved to be comparatively large. For the ortho → meta and meta → para transitions involving gaseous carbaboranes, they are almost identical and amount to ~ -17 kcal mole^{-1}. According to the authors, this suggests that the *para*-isomer is much more stable than the meta-isomer and the latter is more stable than the *ortho*-isomer. The enthalpies of cyclisation of dialkyl-(γ-aminopropyl)-boranes also proved to be large. The enthalpy in the liquid state is -18 kcal mole^{-1}, which accounts for the existence of cyclic compounds, while the corresponding acyclic compounds cannot be isolated. The strain in a five-membered ring with two heteroatoms, namely B and N and B and O, has been estimated as 6 ± 2 kcal mole^{-1}, which agrees with the strain energy in cyclopentane (according to the authors, due to the similarity of the atomic radii of C, O, N, and B).

Table 2. The enthalpies of combustion and formation of organoboron compounds at 298.15 K.[15,17]

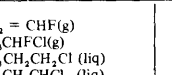
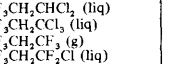
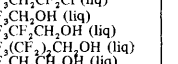
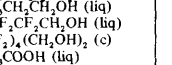
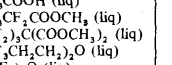
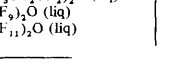
Compound	$-\Delta H°_c$, kcal mole^{-1}	$-\Delta H°_f$, kcal mole^{-1}
o-$B_{10}C_2H_{12}$ (c)	2148.0±1.6	42.4±3.5
m-$B_{10}C_2H_{12}$ (c)	2131.1±1.5	59.3±3.4
p-$B_{10}C_2H_{12}$ (c)	2114.4±1.8	76.0±3.6
1-CH_3-o-$B_{10}C_2H_{11}$ (c)	2291.1±1.3	60.8±3.9
1,2-$(CH_3)_2$-o-$B_{10}C_2H_{10}$ (c)	2446.7±1.9	68.4±3.6
1-(CH_2OH)-o-$B_{10}C_2H_{11}$ (c)	2270.0±1.7	82.7±3.5
1-(COOH)-o-$B_{10}C_2H_{11}$ (c)	2153.3±2.0	131.1±3.7
$(n\text{-}C_3H_7)_2BN(n\text{-}C_3H_7)_2$ (liq)	2140.2±1.4	104.1±1.4
$(n\text{-}C_4H_9)_2BN(n\text{-}C_4H_9)_2$ (liq)	2766.8±1.6	126.9±1.6
	1617.7±2.2	71.1±2.2
	1615.8±1.7	73.1±1.7
	1682.1±2.0	75.1±2.0
	1988.4±2.0	93.5±2.1
	2003.8±1.6	78.1±1.6
	1222.4±0.7	107.6±0.7

Table 3. The enthalpies of formation of tricyclopentadienyl-lanthanide complexes[19] at 298.15 K.

Compound	$\Delta H°_f$, kcal mole^{-1}	Compound	$\Delta H°_f$, kcal mole^{-1}
$Sc(C_5H_5)_3$ (c)	−3,2±1	$Pr(C_5H_5)_3$ (c)	−6.7±2
$Y(C_5H_5)_3$ (c)	−10.8±1	$Tm(C_5H_5)_3$(c)	−11.8±1
$La(C_5H_5)_3$(c)	−6.4±1	$Yb(C_5H_5)_3$ (c)	7.0±1

The enthalpies of combustion and formation of 38 organic compounds of transition metals [tricyclopentadienyl-lanthanides (Table 3); dicyclopentadienyl compounds of metals of the 3*d* series; dicyclopentadienyl complexes of molybdenum, tungsten, zirconium, and hafnium hydrides, chlorides, and iodides (Table 4); alkylcyclopentadienyl and cyclopentadienyl phenyl compounds of titanium, zirconium, and platinum; arene derivatives of chromium; niobium and tantalum alkoxides (Table 5)] were determined by Rabinovich, Tel'noy, and coworkers at the Termochemical Laboratory of Gorky

State University[18–25]. The purity of these compounds was 99.97–99.99%. Special measures were taken to prevent their oxidation before combustion. The solid combustion products were determined chemically and by X-ray diffraction. The error of the determination of the enthalpy of combustion was 0.02–0.05%.

Table 4. The enthalpies of formation of dicyclopentadienyl complexes of metals of the 3*d* series[20,23] at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}
$(C_5H_5)_2Cr$ (c)	42.7±0.5
$(C_5H_5)_2Mn$ (c)	48.0±0.5
$(C_5H_5)_2Fe$ (c)	40.2±0.4
$(C_5H_5)_2Co$ (c)	56.5±0.5
$(C_5H_5)_2Ni$ (c)	68.2±0.4
$(C_5H_5)_2MoH_2$ (c)	46.6±0.6
$(C_5H_5)_2WH_2$ (c)	59.9±0.6
$(C_5H_5)_2ZrCl_2$ (c)	−128.1±0.6
$(C_5H_5)_2HfCl_2$ (c)	−128.6±0.7
$(C_5H_5)_2MoCl_2$ (c)	−22.9±0.6
$(C_5H_5)_2WCl_2$ (c)	−17.0±0.6
$(C_5H_5)_2MoI_2$ (c)	7.2±0.5
$(C_5H_5)_2WI_2$ (c)	28.0±0.7

Table 5. The enthalpies of formation of a number of transition metal compounds[21,23,25] at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}
$(C_5H_5)_2Ti(CH_2C_6H_5)_2$ (c)	46.8±1.2
$(C_5H_5)_2Zr(CH_3)_2$ (c)	−10.6±0.5
$(C_5H_5)_2Zr(C_6H_5)_2$ (c)	65.9±2.6
$(C_5H_5)Pt(CH_3)_3$ (c)	40.3±0.5
$(C_5H_5)_2Pt(CH_3)_2$ (c)	31.2±1.7
$(C_6H_5C_2H_5)_2Cr$ (liq)	15.9±1.0
$[C_6H_4(C_2H_5)_2]_2Cr$ (liq)	−11.3±1.9
$[C_6H_4(C_3H_7)_2]_2Cr$ (liq)	−46.7±2.0
$(CH_3O)_5Nb$ (liq)	337.9±0.6
$(C_2H_5O)_5Nb$ (liq)	378.6±0.6
$(C_3H_7O)_5Nb$ (liq)	406.7±0.9
$(CH_3O)_5Ta$ (liq)	338.8±0.6
$(C_2H_5O)_5Ta$ (liq)	391.6±0.7
$(C_3H_7O)_5Ta$ (liq)	420.5±1.0

The enthalpies of formation of the above substances in the condensed state and the data in Refs. 18–25 or those of other workers for the enthalpies of sublimation or vaporisation were used to calculate the enthalpies of formation in the gaseous state and from the latter the average dissociation energies of many bonds formed by transition metals in their organic derivatives were calculated. Together with the results of calculations from thermochemical data in the literature for metal carbonyls and several alkoxides, these results are presented in Figs. 1–3.[23] In all cases the average dissociation energy of the M–L bond in the compounds ML_n with the same ligand and identical values of n increases down the Groups of the Periodic System as the atomic number of the metal increases. This is particularly interesting in view of the fact that the opposite variation has been observed for organic derivatives of non-transition elements (E) — the average dissociation energy of E–R bonds decreases in the compounds ER_n with the same R and n down the Groups of the Periodic System as the atomic number of the element increases (Fig. 4).[26] Clearly this behaviour of transition metal compounds is due to the specific features of the variation of their effective nuclear charge and of the configuration of the electron shell in the subgroups of the Periodic System. We established that similar opposed variations are observed also for inorganic compounds of transition and non-transition elements[26].

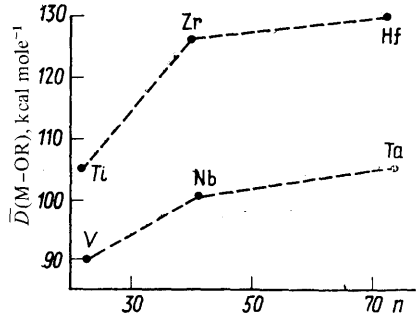


Figure 1. Dependence of the dissociation energy of M–OR bonds in transition metal alkoxides on the atomic number of the metal n.[26]

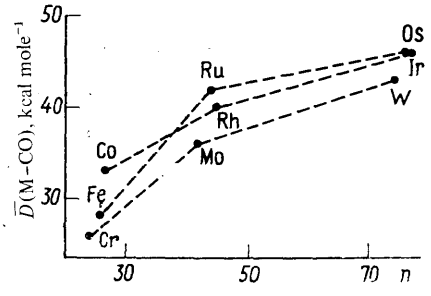


Figure 2. Dependence of the average dissociation energy of the M–CO bonds in metal carbonyls on the atomic number of the metals n.[26]

The enthalpies of combustion and formation of a further 54 organic compounds of metals, including 24 different silicon compounds, some of which are listed in Table 6, 14 germanium compounds (Table 7), and certain tin, aluminium, mercury, and magnesium compounds have been measured in the USSR. Most of these studies were carried out in Kostryukov's[27–30], Gadzhiev's[31–33], Shaulov's[34–42],

and the author's[43–47] laboratories. Tel'noy and Rabinovich wrote a review of the Soviet and foreign studies on the thermochemistry of organic compounds of transition metals[23].

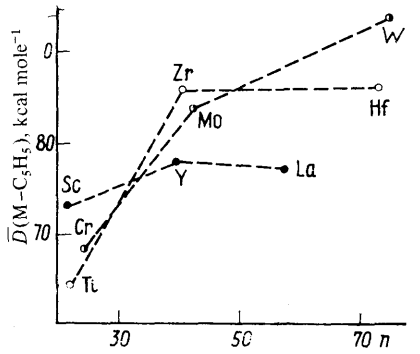


Figure 3. Dependence of the average dissociation energy of the M–C_5H_5 bonds in dicyclopentadienyl derivatives of transition metals on the atomic number of the metal n.[26]

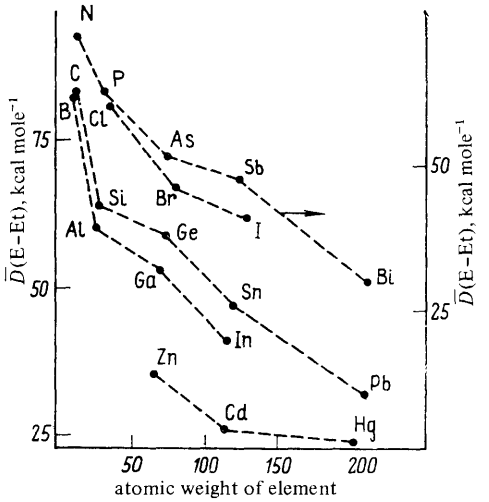


Figure 4. Dependence of the average dissociation energy of the element (E)–ethyl group (Et) bonds in the compounds EEt_n of non-transition elements on the atomic number of the element n.[26]

The enthalpies of combustion and formation of ~100 organic nitrogen compounds of different classes have been determined in Lebedev's[48–52] and Lebedeva's[53–57] laboratories. These are nitrohydrocarbons, alkylamines, amides, and nitriles, nitro- and amino-acids, as well as other compounds which are of considerable theoretical and applied interest. Finally, in this section we may mention studies on non-aromatic bicyclic and polycyclic compounds, which are being carried out systematically by Kozina and Gal'chenko at Moscow State University[58–60]. Together with their coworkers, they determined the enthalpies of combustion and formation of ~15 substances belonging mainly to the bicyclo[2,2,1]heptane (norbornane) and bicyclo[4,1,0]heptane (norcarane) series (Table 8). The energetics of these compounds are of considerable theoretical interest and some of them are used in industry.

Table 6. The enthalpies of formation of a number of organosilicon compounds at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}	Refs.
$(C_2H_5)_3SiN(C_2H_5)_2$ (liq)	−88±1	43
$(CH_3)_2(C_2H_5O)Si(CH_2)_3NH_2$ (liq)	−154±2	35
$[(C_2H_5)_2N]_2SiH$ (liq)	−131±1	43
$(CH_3)_3SiOOC(CH_3)_3$ (c)	−126±3	44
$(C_2H_5)_6Si_2Hg$ (liq)	−40±1	45
CH_3SiCl_3 (liq)	−145.5±1.1	31
$(CH_3)_2SiCl_2$ (liq)	−116.8±0.8	31
$(CH_3)HSiCl_2$ (liq)	−104.0±1.0	31
$(C_2H_5)_4Si$ (liq)	56.8±1.7	31
$(C_6H_5)_2SiCl_2$ (liq)	−48.2±2.7	
$(C_6H_5)_3SiCl$ (c)	12.5±4.1	31

Table 7. The enthalpies of formation of a number of organogermanium compounds at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}	Refs.
$(CH_3O)_4Ge$ (liq)	205.5±0.4	39
$(C_2H_5O)_4Ge$ (liq)	244.8±0.5	39
$(C_6H_5O)_4Ge$ (liq)	112.7±1.0	39
$(C_2H_5)_6Ge_2O$ (liq)	148±4	44
$(C_2H_5)_3GeOOC(CH_3)$ (liq)	120.4±1.3	44
$(n\text{-}C_4H_9)_4Ge$ (liq)	91.7±1.2	37
$(C_2H_5)_3GeN(C_2H_5)_2$ (liq)	86±1	43
$[(CH_3)_2GeO]_4$ (c)	378.7±1.5	27
$[(C_2H_5)_2GeO]_4$ (c)	379.8±5.2	29
$(C_2H_5)_6Ge_2Hg$ (liq)	32±1	45
$(C_3H_7)_6Ge_2Hg$ (liq)	74±1	45

In all, the enthalpies of formation of ~95 organic derivatives of metals were determined in the Soviet Union during 1971–1975, while in other countries similar determinations were made for altogether ~120 compounds.

III. THE LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS

The temperature dependence of the heat capacities of 12 organoelemental compounds, including seven cyclopentadienyl derivatives of transition metals of the 3*d* series, in the range 5–300 K,[60–62], and 17 alkyl, carbonyl, and bisarene derivatives of metals in the range 60 to 300 K[60–62] were determined by Nistratov, Shaiman, and Maslova at the Thermochemical Laboratory of Gorky University. The thermodynamic functions of the above substances were calculated and the parameters of fusion

and transitions in the solid state were determined. Table 9 lists the entropies of the organoelemental compounds calculated from the temperature variation of the heat capacity.

Table 8. The enthalpies of formation of hydrocarbons of the norbornane and norcarane series[57–59] at 298.15 K.

Hydrocarbon	ΔH_f^0, kcal mole^{-1}	Hydrocarbon	ΔH_f^0, kcal mole^{-1}
cis, cis-Cycloocta-1,5-diene (liq)	13.78±0.33	7,7-Dimethylnorbornane (s)	−35.43±0.39
cis-Carane (liq)	−27.72±0.55	Nortricyclene (s)	7.42±0.27
trans-Carane (liq)	−28.33±0.61	Norbornene (s)	9.89±0.34
3-Carene (liq)	−7.06±0.45	7-Methylenenorbornane (liq)	4.7±0.5
2-Carene (liq)	−5.41±0.57	Camphene (s)	−18.01±0.53

Table 9. Thermodynamic functions of organoelemental compounds at 298.15 K[60–62] (calculations based on the heat capacities measured in the range 5–300 K)

Compound	$H^\circ(298.15) - H^\circ(0)$, kcal mole^{-1}	S°, kcal mole^{-1}	Compound	$H^\circ(298.15) - H^\circ(0)$, cal mole^{-1} K^{-1}	S°, cal mole^{-1} K^{-1}
$Hg(C_5H_5)_2$	10.28	67.44	$Mn(C_5H_5)_2$	8.34	60.08
$In(C_5H_5)_3$	14.55	88.67	$Co(C_5H_5)_2$	7.81	56.42
$Si(C_5H_5)_4$	15.52	98.44	$Ni(C_5H_5)_2$	8.25	60.47
$As(C_5H_5)_3$	12.90	84.48	$(C_5H_5)_2Ti(OCOC_6H_5)_2$	18.59	129.9
$V(C_5H_5)_2$	7.92	57.40	$(C_5H_5)_2HfCl_2$	10.27	73.27
$Cr(C_5H_5)_2$	7.71	56.40	$(C_5H_5)_2CrI$	10.18	74.54

Fairly distinct λ-transitions in the solid state were observed in the dicyclopentadienyl derivatives of vanadium, chromium, cobalt, and nickel; like the transitions known previously for ferrocene[63], these are transitions of the order–disorder type and are due to the manifestation of the hindered rotation of the ligands ‡. (Fig. 5 illustrates the λ-transitions in chromocene and cobaltocene).

‡ The rotation of the cyclopentadienyl rings, which alters their mutual intramolecular orientation, causes a significant change in the energy of the interaction of the rings of neighbouring molecules in the crystal lattice.

It is striking that the above compounds can be arranged in a series in terms of the enthalpies of the transitions (Table 10), which differs little from the series based on the absolute negative charges on the metal atoms, calculated by Armstrong et al.[64] The ratios of the hindered and eclipsed conformations of the molecules in each of the above four compounds were determined from the enthalpies of the transitions (Table 10). Here $\Delta S_t = R \ln X < R \ln 2$, where $X = 1.39$, 1.36, 1.17, and 1.16 for the cobalt, chromium, nickel, and vanadium compounds respectively ($X = 1.89$ for ferrocene).

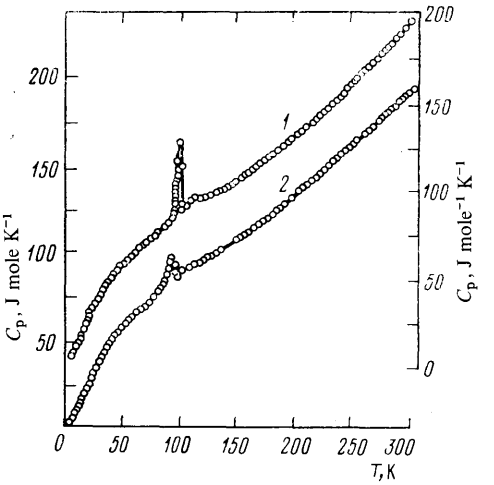


Figure 5. Occurrence of the λ-transitions in solid chromocene (curve *1*) and cobaltocene (curve *2*) on the curves representing the temperature variation of their heat capacities[65].

Table 10. Parameters of the λ-transitions of dicyclopentadienyl derivatives of transition metals of the 3*d* series[62].

Compound	T, K	ΔH_t^0, cal mole^{-1}	ΔS_t^0, cal mole^{-1} K^{-1}
$Fe(C_5H_5)_2$*	125—200	204	1.27
$Cr(C_5H_5)_2$	75—140	63.3±0.8	0.61±0.01
$Co(C_5H_5)_2$	70—120	56.8±0.5	0.65±0.01
$V(C_5H_5)_2$	120—200	46.8±0.5	0.29±0.01
$Ni(C_5H_5)_2$	100—190	43.4±0.5	0.32±0.01

* Data of Edwards et al.[63] (quoted for comparison with the parameters of the λ-transitions of other 3*d* metals).

It is of interest that the entropy of the λ-transition in dicyclopentadienyltitanium dibenzoate[65] proved to be $\sim R \ln 4$ ($\Delta S_t = 2.75$ cal mole^{-1} K^{-1}), which corresponds to the presence of four molecular conformations above the transition temperature, while there is only one conformation below this temperature. Presumably, two of the four conformations arise owing to the hindered rotation of the cyclopentadienyl rings and two are due to the rotation of the benzoate groups ($\Delta H_t = 392.5$ cal mole^{-1}).

The Gibbs free energies of the direct synthesis of the dicyclopentadienyl derivatives of metals of the 3*d* series as well as their thermal decomposition reactions, which are of interest for the preparation of the pure metals, were calculated from the enthalpies and entropies of formation of the compounds. Fig. 6 shows that the points of intersection of curves *1–6* with curves *7* and *8* determine the lower limits of the temperature ranges in which the above reactions are allowed for different metals at the standard pressure. It is therefore of interest that the coworkers of Academician G. A. Razuvaev (Institute of Chemistry of the USSR Academy of Sciences, Gorky) carried out direct syntheses of a number of cyclopentadienyl and arene derivatives from gaseous metals and solid hydrocarbons *in vacuo* at the temperature of liquid nitrogen[66] on the basis of analogous calculations using the data in Refs. 61–63.

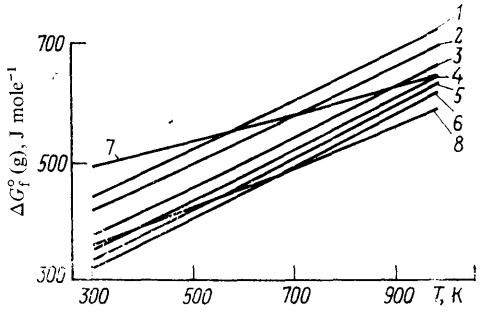


Figure 6. Graphical determination of the temperature ranges in which the reactions $M(g) + 2C_5H_6(g) \rightarrow (C_5H_5)_2.M(g) + H_2(g)$ and $(C_5H_5)_2M(g) \rightarrow M(g) + 2C_5H_5(g)$ at a pressure of 101.325 kPa are thermodynamically allowed (according to the Gibbs free energies of formation of the reactants)[65]: *1)–6)* $M(C_5H_5)_2$; M: *1)* Ni; *2)* Co; *3)* Mn; *4)* Cr; *5)* Fe; *6)* V; *7)* $2C_5H_5$; *8)* C_5H_6.

Kostryukov, Karasharli, and coworkers[67–69] investigated the temperature dependence of the heat capacities and calculated the thermodynamic functions in the range 12–370 K for 13 organosilicon compounds (siloxanes, silacyclanes, and silanes), some of which are listed in Table 11. Anomalies in the solid state, associated either with the deformation of the ring made up of silicon–oxygen bonds or with the hindered rotation of the methyl groups, have been found for a number of the above compounds.

Among other studies, mention should be made of investigations of the heat capacities of a number of benzene derivatives in the gaseous state [300–670 K, 10^5 (5–250) Pa] carried out by Akhundov[70] with the aid of an adiabatic flow calorimeter (error of the measurements ~0.45–0.65%), Kolesov's measurements of the low-temperature heat capacities of chlorofluoropropanes[71], and Paukov's studies on the heat capacities of substituted hexafluorobenzenes[72]. Altogether, in the period under consideration studies were made on the low-temperature heat capacities of ~70 organic compounds; among these ~50 compounds were investigated in the temperature range from 5–12 K to 300 K.

Approximately 30 studies were devoted to the calculation of the thermodynamic functions of organic compounds in the ideal gas state from molecular constants. Among them, special mention should be made of the research by Shaulov[73,74] and Pashinkin and coworkers[75] on the calculation of the thermodynamic functions of alkyl derivatives of Group III–V elements and certain carbonyls used to prepare pure metals and semiconducting compounds.

Clearly the determination of the entropies of ~100 important compounds will be useful for the corresponding technological calculations.

Table 11. Thermodynamic functions of organosilicon compounds[67–69] (calculated from the temperature variation of the heat capacities).

Compound	$H^\circ(298.15)-H^\circ(0)$, kcal mole^{-1}	$S^\circ(298.15)$ kcal mole^{-1} K^{-1}
$(CH_3)_2SiO[(CH_3)_2SiO]_2(CH_3)_2SiO$	16.71	101.4
$(CH_3)_2SiO[(CH_3)_2SiO]_2(C_6H_5)_2SiO$	24.81	181.3
$(CH_3)C_6H_5SiO[(CH_3)C_6H_5SiO]_2(CH_3)C_6H_5SiO$	23.41	158.4
cis-$(CH_3)C_6H_5SiO[(CH_3)C_6H_5SiO](CH_3)C_6H_5SiO$	20.34	136.5
trans-$(CH_3)C_6H_5SiO[(CH_3)C_6H_5SiO](CH_3)C_6H_5SiO$	19.81	131.1
$(CH_3)Si(CH_2)_2CH_3$	10.24	68.8
$(CH_3)SiCH_2Si(CH_3)_2CH_2$	10.99	70.9
p-$Cl_3SiC_6H_5$	11.29	78.6
Cl_3SiCH_2CN	8.47	58.8

IV. THERMODYNAMICS OF POLYMERISATION AND POLYCONDENSATION PROCESSES

In connection with the needs of the rapidly developing polymer industry, a comparatively large amount of research has been done into the thermodynamics of the processes involving the synthesis of polymers. The enthalpies, entropies, and Gibbs free energies of the polymerisation of 20 carbocyclic and heterocyclic substances as well as organometallic compounds have been determined. Most of these studies were carried out by Lebedev and coworkers[76–80] at the Gorky University and in the laboratory of the present author.

It was shown that the polymerisation of certain heterocyclic compounds, which could not be polymerised hitherto, is thermodynamically allowed. This applies particularly to *N*-(β-trimethylsilylethyl)ethyleneimine and the analogous derivative of trimethyleneimine, which are nowadays polymerised indirectly — via complexes with zinc chloride. Table 12 shows that the Gibbs free energies are fairly large and negative for the polymerisation of both the corresponding complexes and the individual imines. Evidently the role of complex formation reduces in these instances to decreasing the process activation energy.

Another heterocycle — 1,1,3,3-tetramethyl-1,3-disilacyclobutane — has been polymerised catalytically near the standard temperature. Cyclopentene and cyclo-octa-1,5-diene also polymerise, giving rise to new varieties of synthetic rubber, glycolide forms a polymer which is used for medical purposes, and tetrahydrofuran polymerises

Table 12. Thermodynamic parameters of the polymerisation of *N*-(β-trimethylsilylethyl)-ethyleneimine and *N*-(β-trimethylsilylethyl)trimethyleneimine directly and via complexes with zinc chloride at 298.15 K.[78]

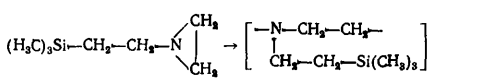
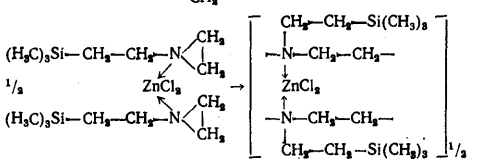
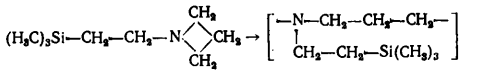
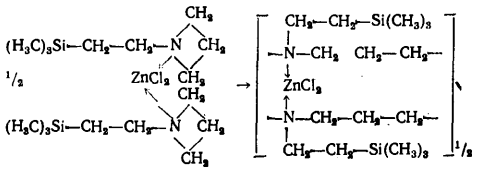
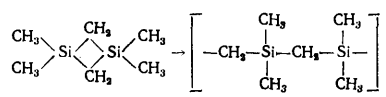
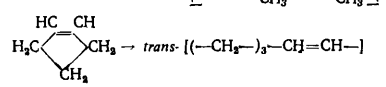
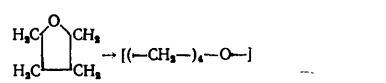
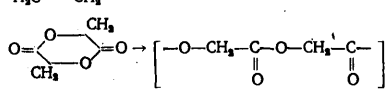
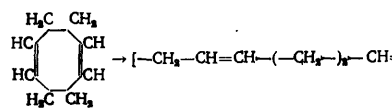
Process	State of reactants	$-\Delta H^\circ$, kcal mole^{-1}	$-\Delta S^\circ$, cal mole^{-1} K^{-1}	$-\Delta G^\circ$, kcal mole^{-1}
	liq → v-e	28.4	24.0	21.2
	c → v	31,5	3.56	30.4
	liq → v-e	27,5	19.9	21.6
	c → v	30.8	4.42	29.5

Table 13. Thermodynamic parameters of the polymerisation of certain cyclic compounds[80] at 298.15 K.

Process	*T*, K	State of reactants	$-\Delta H^\circ$, kcal mole^{-1}	$-\Delta S^\circ$, cal mole^{-1} K^{-1}	$-\Delta G^\circ$, kcal mole^{-1}
	298.15	liq → v-e	17,7	0.90	18.0
	298.15	liq → v-e	4,45	11.0	1.17
	298.15	liq → v-e	4,45	11.4	1.05
	550	liq → v-e	7,51	4.18	5.21
	298.15	liq → v-e	9.56	10.8	6.34

(Table 13). In all cases the polymerisation reaction takes place with ring opening and, in the absence of transitions involving different states of aggregation, the enthalpy of the process is close to the ring strain energy.

In the studies described the enthalpy of polymerisation was determined directly in a calorimeter or calculated from the experimental enthalpies of combustion of the polymers and monomers. The entropy of polymerisation was calculated from the temperature dependence of the heat capacities of the polymers and monomers measured from 4 or 8 K. Specimens of several of these polymers had a comparatively high degree of crystallinity: 40% for the polypentenamer, 65% for polytetrahydrofuran, and 67% for polyglycolide. The difference between the zero-point entropies of the polymers in the amorphous and crystalline states was calculated in these cases from plots of the temperature variation of the heat capacities of the fully crystalline and fully amorphous polymers obtained by extrapolating the corresponding experimental plots for the partly crystalline specimens[81]. For the polymers indicated above, the difference proved to be 3.5–4 cal mole^{-1} K^{-1}, which corresponds to approximately half the entropy of fusion of the above compounds under the conditions of 100% crystallinity. As an example, Fig. 7 presents the temperature dependence of the heat capacity of polytetrahydrofuran used to calculate the entropy.

Together with polymerisation reactions, the thermodynamics of the two-stage polycondensation synthesis of a number of polyheteroarylenes, distinguished by a comparatively high thermal stability, was investigated by Karyakin and coworkers[82–88] at the Thermochemical Laboratory of Gorky State University in collaboration with the laboratory of Academician V. V. Korshak (Institute of Organoelemental Compounds of the USSR Academy of Sciences) and the "Plastics Union". The first stage of the synthesis of these heterocyclic polymers consists in the interaction of aromatic diamines or their derivatives with acid dianhydrides in *N,N*-dimethylformamide with formation of an incompletely cyclised prepolymer. The enthalpies of these reactions were determined directly in an adiabatic calorimeter and their entropies were calculated from measurements of the heat capacities of solutions of each reactant in dimethylformamide as a function of temperature at concentrations corresponding to the polycondensation reactions. In all cases, differing in the composition of the initial amines and anhydrides, the standard Gibbs free energies of the processes at ~298 K show that their equilibria are almost completely displaced towards the formation of the prepolymers.

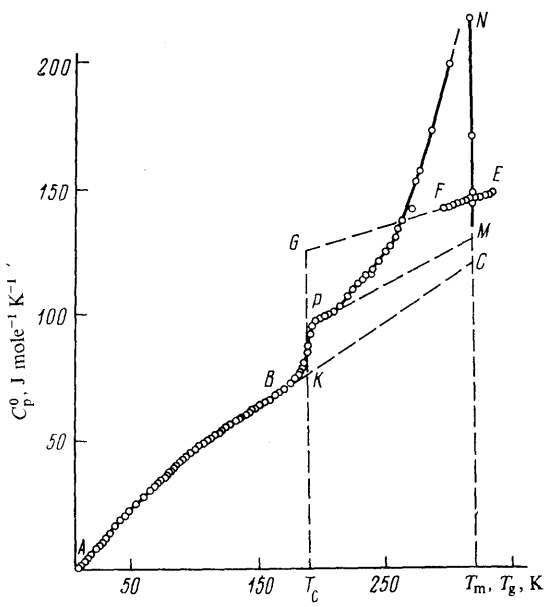
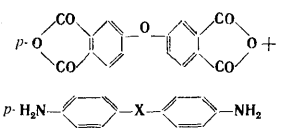


Figure 7. Temperature variation of the heat capacity of polytetrahydrofuran[80]: circles — experimental data for the polymer with a 65% degree of crystallinity; *ABKC*— experimental data for the polymer with 100% degree of crystallinity (extrapolation neglecting the difference between the heat capacities of the amorphous and crystalline polymers before devitrification); *ABPM*— experimental data for the specimen with a 65% degree of crystallinity (extrapolation); *ABGFE*— experimental data for the specimen with 0% degree of crystallinity (extrapolation); T_g and T_m are the glass and melting points respectively.

The second stage of the synthesis involves additional cyclisation of the prepolymer at elevated temperatures with evolution of water. The equilibrium constants of the cyclodehydration reaction were determined from the equilibrium vapour pressure and their temperature variation was used to find the enthalpies of the reactions. The results show that the thermodynamic criteria allow the cyclodehydration of the prepolymers to go virtually to completion over a wide temperature range. However, the reaction does not go to completion because of kinetic factors and the copolymers formed have both the final cyclic structures and the structures of the initial prepolymers. A method has been proposed for the determination of the compositions of such copolymers from their enthalpies of combustion. As an example, Tables 14 and 15 present the thermodynamic parameters of the reactions involving the formation of certain prepolymers and final polymers.

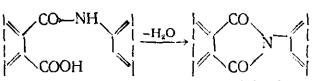
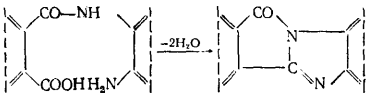
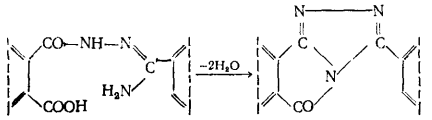
Table 14. Thermodynamic parameters of polycondensation reactions[83]:



(298.15 K; solvent — dimethylformamide)

X	$-\Delta H^\circ$, kcal mole^{-1}	$-\Delta S^\circ$ cal mole^{-1} K^{-1}	$-\Delta G^\circ$, kcal mole^{-1}
O	30.8	46.0	17.1
O—Ph—O	30.5	—	—
—	29.4	—	—
CO	25.3	—	—
SO_2	24.0	45.5	7.4

Table 15. The enthalpies and Gibbs free energies of the cyclodehydration of prepolymers[88] at 400 K.

Reaction	ΔH°, kcal mole^{-1}	$-\Delta G^\circ$, kcal mole^{-1}
 poly(-*p,p'*-diphenyl oxide-) pyromellitimide — polyimide	15.2	7.05
 polyamino-amidoacid — polybenzoylene-benzimidazole	14.9	27.0
 poly(-O-carboxybenzyl-amidrazone) — polybenzoylene-*s*-triazole	23.5	27.9

V. THERMODYNAMICS OF REACTIONS OF PRODUCTS OF PETROCHEMICAL SYNTHESIS AND OTHER PROCESSES

In a number of higher educational establishments of the USSR studies have been made on the thermodynamics of ~150 isomerisation reactions of alkanes, alkenes, and their halogeno-derivatives (the results of some of these are listed in Table 16), the dehydrohalogenation reactions of halogeno-derivatives of alkanes and alkenes, and disproportionation reactions of alkenes. Rozhnov[89–92] (Kuibyshev Polytechnic Institute), Andreevskii and Kabo[93–96] (Belorussian State University), Vasil'eva and coworkers[97] (All-Union Petrochemical Synthesis Institute), and others studied experimentally the equilibria in the processes in the range from the standard temperature to 600 K and calculated the thermodynamic parameters of the reactions from their equilibrium constants and the temperature variation of the latter. Some of the processes investigated are already used in industry and others can be so employed. Particular mention should be made of the determinations, which are of practical importance, of the thermodynamic parameters of a number of reactions involving the pyrolysis of benzene[98], the synthesis of 4,4-dimethyl-1,3-dioxan from isobutene and formaldehyde and its conversion into isoprene[99], and the synthesis of alkylene carbonates[97] and Freon-11 and Freon-12,[100] as well as the investigation of the equilibria in the individual stages of the formation of isoprene and piperylene from isopentene[101], etc.

Table 16. The enthalpies and entropies of isomerisation of alkanes, alkenes, and their halogeno-derivatives[92–96].

Reaction	Conditions	$\overline{\Delta H^\circ}$, kcal mole^{-1}	$\overline{\Delta S^\circ}$, cal mole^{-1} K^{-1}
$CH_2Br-CH_2-CH_3 \rightleftarrows CH_3-CHBr-CH_3$	273–583 K; (liq)	−2.86±0.13	−3.66±0.38
$CH_2Br-CH(CH_3)-CH_3 \rightleftarrows CH_3-CBr(CH_3)-CH_3$	273–526 K; (liq)	−3.800±0.160	−5.8±0.5
$CH_3Cl-CH_2-CHCl-(CH_2)_2-CH_3 \rightleftarrows CH_3Cl-(CH_2)_2-CHCl-CH_2-CH_3$	273–363 K; (liq)	−0.530±0.030	0.90±0.09
erythro-$CH_3-CHCl-CHCl-CH_3 - CH_3 \rightleftarrows$ *meso*-$CH_3-CHCl-CH_2-CHCl-CH_3$	273–373 K; (liq)	1.890±0.100	2.43±0.32
$CH_2=C(CH_3)-(CH_2)_2-CH_3 \rightleftarrows CH_3-C(CH_3)=CH-CH_2-CH_3$	273–516 K; (gas) 101 кПа	−1.13±0.15	−0.30±0.35
$CH_3-CCl(CH_3)-CH_2-CH_3 \rightleftarrows CH_3-CH(CH_3)-CHCl-CH_3$	273–373 K; (liq)	1.89±0.05	1.75±0.2

Research into the thermochemistry of the complex formation reactions of organic compounds is being rigorously prosecuted in our country. Gur'yanova and Gol'dshtein and coworkers (Karpov Physicochemical Institute) investigated the formation of complexes by ethers, sulphides, selenides, amines, phenols, and organophosphorus compounds with alkyl derivatives of boron and aluminium, the halides of various elements, and other substances (for further details, see the monograph of Gur'yanova et al.[102]).

In the Thermochemical Laboratory of Gorky State University, Tsvetkov and coworkers carried out a series of studies on the thermochemistry of the interaction of alkyl derivatives of Group III–V elements with one another[103,104]. The corresponding complexes are of interest, because semiconducting compounds can be obtained from them. A large number of studies on the thermochemistry of hydrogen-bonded complexes have been described in detail in a recent review[105].

VI. LIQUID–VAPOUR EQUILIBRIA INVOLVING PURE SUBSTANCES

Data on the vapour pressures and enthalpies of vaporisation and sublimation of ~500 substances (the studies by Karapet'yants and coworkers on the precision measurements and approximate calculation of the vapour pressures of many organosilicon, organotin, and organogermanium compounds[106–108], a number of studies on the vapour pressures of linear and cyclic oligo-organosiloxanes and other organosilicon compounds with different substituents at the silicon atom[109,110], studies by Gal'chenko and Lebedev and coworkers on the direct determination of the enthalpies of sublimation of organoboron compounds[111], studies by Devyatykh and coworkers on the vapour pressures of cyclopentadienyl derivatives of the lanthanides[112], studies by Rabinovich, Kir'yanov, and coworkers on the vapour pressure of cyclopentadienyl derivatives of transition metals of the 3*d* series[20,21], studies by Baev at the Belorussian Technological Institute on the vapour pressures of alkyl derivatives of non-transition elements[113] and metal carbonyls[114], as well as those of many other investigators) were published in 1971–1975.

It is clear from the list of compounds whose vapour pressures have been investigated that they are of both theoretical and applied interest. In particular, the enthalpies of vaporisation and sublimation obtained have been used in a number of investigations to calculate the enthalpies of formation of compounds in the gaseous state from their experimental enthalpies of formation in the condensed state §.

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Exciting Developments in the Thermophysics of the Pnictides and Chalcogenides of the Transition Elements

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A terse reexamination of the thermophysical aspects of the chemical thermodynamics of the transition element chalcogenides is presented with a view to updating the Grønvold and Westrum approach of 1962. A somewhat more detailed progress report and insight into the situation pertaining to the transition element pnictides is also pursued in order to attain an impression of the similarities and differences between these two important classes of transition element compounds.
The increasing availability of high-temperature adiabatic calorimetric data to supplement that obtained by cryogenic calorimetry, a better appreciation of the dilatometric contribution (especially important as higher temperatures are considered), the effect of band structure and related problems are reviewed, and interesting examples of these and other phenomena are presented for a few selected substances including marcasite, cobalt ditelluride, iron diantimonide, chromium diantimonide, chromium monoarsenide, triuranium tetraarsenide and tetraantimonide, uranium diantimonide, diarsenide, and low-digenite ($Cu_{1.80}S$).
The bibliography includes 90 references.

CONTENTS

I.	Perspective and introduction	1186
II.	Contributions to the heat capacities	1187
III.	Calorimetric technique	1188
IV.	Marcasite/pyrite metastable transformation	1188
V.	Cobalt ditelluride and cobalt diselenide	1189
VI.	Thermophysical properties of $FeSb_2$	1190
VII.	Chromium diantimonide	1190
VIII.	Chromium monoarsenide	1191
IX.	Actinide pnictides	1192
X.	The copper - sulphur system	1194

At the very outset I would like to express my appeciation to the Organizing Committee of the All-Union Conference on Calorimetry (Moscow, 1977) and to the Academy of Sciences of the U.S.S.R. for providing this opportunity for us to meet together and to discuss progress on thermodynamic projects of mutual concern. I can remember well my first participation in the third of these impressive meetings and in the intervening conferences as well and hope that there will be many more as it is clearly to the mutual advantage of the advancement of our projects to learn of new developments—but more important—it results in an accelerated achievement of progress towards our ultimate goals. The excellence of the papers presented and the enthusiasm of the participants attests to the careful planning by the Organizing Committee.

I. PERSPECTIVE AND INTRODUCTION

Approximately a decade and a half ago, Grønvold and Westrum, in the first issue of the then new Journal, "Inorganic Chemistry", presented an extensive paper concerned with the correlation and estimation of the entropies of the transition element chalcogenides[1]. By way of reminder, the most striking outcome of this analysis involved the fact that the cationic entropy contribution according to Latimer[2], instead of increasing gradually and continuously in a monotonic logarithmic aspect, leveled off essentially in "shelves" for each of the successive n-levels of the principal "d" quantum numbers as shown in Fig. 1. Although this approach was not adopted by Mills in his mammoth compilation of the thermodynamics of the sulphides, selenides, and tellurides[3], we are undaunted as to its essential correctness and believe that he did not detect it primarily because he was using equilibrium as well as the direct adiabatic calorimetric determination of entropies and simply did not, therefore, enjoy the same high precision of resolution that was possible to us. As a matter of fact, a recent application of this scheme to the lanthanide halides has done much to verify its essential correctness insofar as the lanthanides are concerned[4,5].

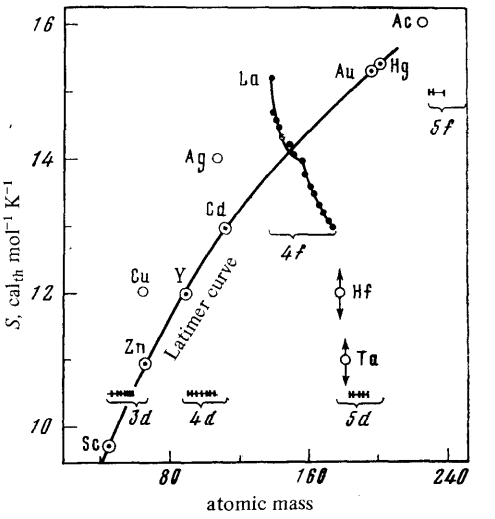


Figure 1. Modification of the Latimer cation scheme for transition[1], lanthanide[6], and actinide[1] elements.

In surveying the progress that has been made in this area subsequent to 1962, we note particularly that more than anything else the era is characterized by a relatively slow accumulation of data on the transition-element chalcogenides. Only within the last two years have F. Grønvold and the author been involved once again in this study and most of this work remains as yet unpublished. Some idea of the recent progress is summarized in Table 1; the most important new development has been the determination of the higher-temperature heat capacities by adiabatic calorimetry done primarily by Grønvold at Oslo.

Table 1. Chalcogenides and pnictides for which Third-Law entropy data have recently been obtained in the author's laboratory.

Chalcogenides				Pnictides		
		3d			*3d*	
FeS_2 (marcasite)	$CoTe_2$	NiS	$Cu_{1.00}S$ (covellite)	CrAs	FeAs	NiAs
	$CoSe_2$		$Cu_{1.75}S$ (anilite)	CrSb		
			$Cu_{1.80}S$ (low-digenite)	$CrSb_2$		
			$Cu_{1.96}S$ (djurleite)		*5f*	
			$Cu_{2.00}S$ (chalcocite)	$ThAs_2$		UAs_2
		4d		$ThSb_2$		USb_2
$RuSe_2$		Ag_2S				U_3As_4
		5f				U_3Sb_4
$ThSe_2$						

In considering a similar (preliminary) survey of the transition element pnictides we find that the availability of high-temperature data is an important aspect. In some ways many of these compounds are more metallic than the corresponding chalcogenides, and band structures replace the convenient discrete electronic levels characteristic of many of the chalcogenides. This involved new problems of interpretation and correlation. At the present time, thermophysical data on a baker's dozen of these have been generated—primarily through our own endeavours—and we continue to pursue enthusiastically these very interesting substances. It is too soon yet to attempt a true overview, but this paper will present some of the interesting developments which have thus far been encountered in both classes of compounds. In the presentation which follows an arbitrary selection of the results has been made to emphasize particularly the interesting phenomena encountered over high- and low-temperature ranges in both chalcogenides and pnictides. Hopefully, the time will soon be ripe for a more detailed analysis and correlation of the pnictides. I want to emphasize that without the great skill in synthesis that has been developed at the Kjemisk Institute at Oslo, initially under Professor Haakon Haraldsen and more recently by Dosent Grønvold, neither temperature range could have been covered with assurance that the materials were "well characterized". The work has been materially accelerated by other collaborators as noted in the acknowledgement.

II. CONTRIBUTIONS TO THE HEAT CAPACITIES

A perpetual endeavour in our studies is first of all to understand the resolution of the heat capacity into the several most important contributions involved. This resolution, based in part upon knowledge of the compound from other auxiliary techniques, is important, not merely as an exercise in itself, but also as a means of enhancing our ability to estimate the thermodynamic properties of transition elements, chalcogenides, and pnictides. We may consider the observed heat capacity to be a sum of the following contributions:

$$C_p = C_v(l) + C(e) + C(m) + C(s) + C(d).$$

Here $C_V(l)$ is the lattice-vibrational heat capacity at constant volume, $C(e)$ the conduction electron contribution, $C(m)$ the cooperative magnetic contribution from population of excited electronic states, $C(s)$ the Schottky contribution, and $C(d)$ the dilation contribution. In transition regions the various contributions may be coupled, but the feasibility of their separation is assumed.

Lattice heat capacity at constant volume. This prime contribution to the heat capacity may usually—in the absence of more detailed information—be expressed by a single Debye function with constant characteristic temperature, Θ_D, for a simple monatomic substance, or by a sum of Debye and Einstein functions for a compound. As a first approximation, the higher-temperature heat capacity is often calculated after evaluating an effective Debye temperature from the heat capacity over the 50 to 100 K region.

Conduction electron contribution. The molar electronic contribution to heat capacity is in the first approximation proportional to the thermodynamic temperature T and equal to

$$C_v(e) = \frac{4\pi^2 k^2 m T N_A}{h^2 (3\pi^2 N/V)^{2/3}} = \gamma T,$$

where k is the Boltzmann constant, m the electron rest mass, L the Avogadro number, h the Planck constant, and N/V the number of electrical carriers per unit volume. The γ's calculated from electrical measurements are, however, often smaller than those derived from low-temperature, heat-capacity measurements.

Magnetic and Schottky contributions [$C(m)$ and $C(s)$]. These contributions often occur either as a cooperative transition from a magnetically ordered state (ferro-, ferri, antiferro-, or heli-magnetic state) or from a gradually changing electron distribution with temperature, i.e. a Schottky transition. For the former case, the magnetic entropy change is related to the changes in the observed magnetic moment or to susceptibility below and above the transition, but the interpretation is still uncertain in most cases. The molar heat capacity from a non-cooperative, Schottky-type transition can be expressed as

$$C(s) = RT\partial^2\{T \ln \Sigma g_i \exp(-E_i/kT)\}/\partial T^2,$$

where g_i is the degeneracy of the ith level, separated from the ground level by an electronic energy E_i. Differentiation yields an expression suitable for computer calculations[6]:

$$C(s) = (1/RT^2)\left[\frac{\Sigma E_i^2 g_i \exp(-E_i/kT)}{\Sigma g_i \exp(-E_i/kT)} - \left\{\frac{\Sigma E_i g_i \exp(-E_i/kT)}{\Sigma g_i \exp(-E_i/kT)}\right\}^2\right].$$

This contribution should by no means be regarded as important only at very low temperatures. Sommers and Westrum have shown it to be important above 300 K also [4,5]. Furthermore, the paper by Rakhmenkulov et al. [7] presented at this meeting has provided much interesting information on lanthanide phosphides.

The dilation contribution. In general, this contribution is

$$C(d) = C_p - C_v = \alpha^2 VT/\beta,$$

where α is the thermal expansivity, V the molar volume, T the thermodynamic temperature, and β the isothermal compressibility. When the thermal expansivity is known, but not the compressibility, the dilation contribution can be estimated by use of the Grüneisen relation:

$$C(d) = \alpha\Gamma C_v T,$$

where the Grüneisen parameter Γ is chosen on the basis of values for related substances. A better estimate is obtained when both α and β have been determined at one and the same temperature but Γ is in general slightly temperature dependent. When neither α nor β is known—the dilation contribution may be estimated according to Nernst and Lindemann as

$$C(d) = AC_p^2 T/T_f,$$

where the "universal" constant $A = 0.005$ J^{-1} K for one gram-atom and T_f is the melting temperature of the substance.

III. CALORIMETRIC TECHNIQUE

Heat capacity measurements were made in a Mark II adiabatic cryostat over the 50 to 300 K region at the University of Michigan. This cryostat was described previously [8]. The samples were contained in gold-plated copper calorimeters which incorporated a gold-gasketed seal and gold-plated copper vanes to enhance conductivity. Temperatures were measured with a platinum, capsule-type, 25-ohm (nominal) resistance thermometer inserted into a re-entrant well in the calorimeter.

The calorimetric apparatus and measuring technique for the region 300 to 1030 K at the University of Oslo have been described [9]. The calorimeter was intermittently heated, and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed silica glass tube of about 50 cm^3 volume, tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum, resistance thermometer.

The cryogenic thermometer had been calibrated by the U. S. National Bureau of Standards, and that for the high-temperature calorimeter locally, at the ice, steam, tin, zinc, and antimony points. Temperatures are judged to correspond to IPTS-68 within 0.03 K from 5 to 300 K and within 0.05 K between this temperature and 900 K. The uncertainty rises to 0.2 K at 1030 K. Resistance, energy, and mass were measured with reference to calibrated instruments by the U. S. National Bureau of Standards.

The heat capacities of both types of empty calorimeters were determined in separate series of experiments. It is emphasized that both sets of measurements were made by adiabatic calorimetry and that equilibrium was typically achieved in all determinations.

IV. MARCASITE/PYRITE METASTABLE TRANSFORMATION

One of our most satisfying publications of 1976 has been the resolution of the stability of marcasite vis-ã-vis pyrite [10]. As is well known, iron disulphide occurs in nature (and can be prepared in the laboratory also) in two polymorphic forms, marcasite and pyrite. While a considerable amount of thermodynamic data exists for pyrite [3,11], such data are virtually unknown for marcasite, except for some measurements of its enthalpy of combustion [12-14]. In order to remedy this situation and to evaluate the stability conditions for the polymorphs, the heat capacity of marcasite has been determined from 5 K to the temperature region where it transforms into pyrite. Measurements on the previously studied pyrite sample [1] have been extended to 770 K.

The heat capacity of the pyrite sample increased gradually over the temperature range 5 to 770 K without any sign of transformation [10]. The values were usually 0.1 to 1.0 per cent lower than for marcasite at the corresponding temperature. The higher-temperature, heat-capacity measurements on marcasite were quite normal until an energy input produced a somewhat higher temperature increment and brought the temperature up to 706.43 K. Here the drift-rate gradually changed from a slightly negative value of about -0.0009 K min^{-1} to large positive values after a period of 2 h. The subsequent gradual temperature increase was followed for a further 96 h, at which time the temperature was estimated to be not more than (0.15 ± 0.25) K from the limiting value T_∞. [15] The enthalpy of transformation of marcasite to pyrite at 700 K is $\Delta H^\circ_{tr} = (-1050 \pm 50)$ cal$_{th}$ mol^{-1}†. When the heat-capacity measurements were continued after 96 h, the heat capacity corresponded closely to that of pyrite, and X-ray powder photographs taken of the sample after completion of the measurements showed the presence only of pyrite.

In the absence of a zero-point entropy in this system, marcasite even in the vicinity of the transformation temperature is thermodynamically metastable with respect to pyrite. Since the transformation is monotropic and irreversible, we cannot ascribe an entropy increment to the transformation and instead utilize an enthalpy cycle for the marcasite-pyrite system through $T = 0$. Taking into account the enthalpy increment for the marcasite to pyrite transformation to 700 K, $H(T = 0,$ marcasite$) - H(T = 0,$ pyrite) is found to be (0.99 ± 0.05) kcal$_{th}$ mol^{-1}. This value should, therefore, be incorporated into $[G^\circ(T) - H^\circ(0)]/T$ for marcasite for chemical thermodynamic calculations. Moreover, marcasite is seen to be clearly metastable with respect to pyrite above $T = 0$. For example, at 298.15 K the value of ΔG° (marcasite → pyrite) is (-0.95 ± 0.05) kcal$_{th}$ mol^{-1}.

Our results together with the critically evaluated values of ΔH_f°(pyrite) from Mills' [3] and from Robie and Waldbaum's [12] reviews together with entropies for iron [16] and sulphur [17] yield the following standard enthalpies, entropies, and Gibbs energies of formation of FeS_2 at 298.15 K:

		Pyrite	Marcasite
$\Delta_f H^\circ$,	kcal$_{th}$ mol^{-1}	-41.5 ± 0.5	-40.5 ± 0.5
$\Delta_f S^\circ$,	cal$_{th}$ K^{-1} mol^{-1}	-9.07 ± 0.10	-8.84 ± 0.10
$\Delta_f G^\circ$,	kcal$_{th}$ mol^{-1}	-38.8 ± 0.5	-37.9 ± 0.5

The geological occurrence of pyrite pseudomorphs after marcasite is consistent with above interpretation, since

† Throughout this paper, cal$_{th}$ = 4.184 J.

marcasite presumably occurs in low-temperature hydrothermal deposits and apparently occasionally transforms into pyrite at temperatures well below 700 K.

V. COBALT DITELLURIDE AND COBALT DISELENIDE

We have determined the heat capacity of another compound of marcasite-type structure—orthorhombic cobalt ditelluride—from 5 to 1030 K by adiabatic-shield calorimetry with intermittent energy inputs and equilibration. It shows interesting behaviour [18].

Its paramagnetism indicates the presence of unpaired 3*d*-electrons. The effective magnetic moment (2.2 μ_B at 720 K) [19] is much smaller than the moment (3.87 μ_B) expected for Co^{2+} in the high-spin state and somewhat higher than the value 1.73 μ_B for the low-spin state in the configuration spin-only approximation. The intermediate moment observed is possibly due to orbital contributions of the kind commonly observed in the case of Co(II) complexes. Hence, the effect of orbital ordering might be observable in the heat capacity of $CoTe_2(m)$ just as predicted [20] for the related ferromagnetic case and observed for $CoS_2(p)$‡.

According to Goodenough [21], $CoTe_2(m)$ contains one itinerant 3*d*-electron in a σ^*-band sufficiently wide to preclude cooperative magnetic ordering. Overlap of this band with a σ^*-band of the anions was suggested as an explanation of the non-stoichiometry of the $CoTe_{2+x}$-phase. The Vandenbempt alternative view [22] presupposes antiferromagnetic ordering in $CoTe_2(m)$, by analogy with the assumption made for $CoSe_2(p)$ by Adachi et al. [23] However, neither the present heat-capacity measurements, nor the Mössbauer experiments by Kjekshus and Nicholson [24] indicate the presence of cooperative ordering or magnetic exchange interactions due to localization of 3*d*-electrons into sub-bands.

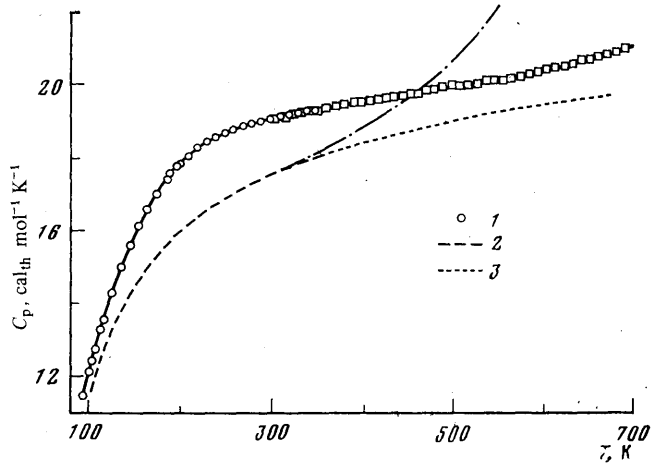


Figure 2. Molar heat capacity of $FeSb_2$ from 100 to 700 K compared with that of $FeTe_2$. ○, Results for $FeSb_2$ from low-temperature calorimetry; □, results for $FeSb_2$ from high-temperature calorimetry; ---, results for $FeTe_2$ by Westrum et al. [25], –·–·–, results for $FeTe_2$ by Mikler et al. [26], ----, extrapolated lattice heat capacity of $FeTe_2$.

‡ *m* = magnetic; *p* = paramagnetic.

No lattice-dynamical analysis has yet been carried out. In analysing the thermophysical properties of $CoTe_2$, we therefore used the experimental heat capacity of $FeTe_2$ [25]—a rate isostructural analogue of $CoTe_2$. This compound is non-magnetic, has semiconducting properties and its atomic masses, interatomic distances, and angles are almost identical with those of $CoTe_2$. Thus, the excess heat capacity of $CoTe_2(m)$ relative to $FeTe_2$ might be related to differences in the outer electronic structure rather than to differences in the lattice contributions. The excess heat capacity rises to a rather pronounced maximum of 1.7 cal_{th} mol^{-1} K^{-1} at 80 K and then falls gradually with increasing temperature. It may reflect a large increase in density of states just above the Fermi level, and thus the presence of levels or bands with high-density regions which presumably derive from the broader bands assumed by Goodenough [21] and by Vandenbempt et al. [22] In the absence of further details about the level and band structure of $CoTe_2(m)$, it remains to be investigated whether the lowest excited level or band is primarily an antibonding σ^*-metal state, an overlapping-anion, *p*-band state, or of other origin.

The resemblance of the excess heat capacity to a Schottky-type transition is illustrated in Fig. 2 on the assumption of two excited levels 65 and 175 cm^{-1} above the ground level with degeneracies $g_0 : g_1 : g_2 = 1 : 1 : 3$. The rather good fit in the region up to 100 K cannot be taken as a proof of the uniqueness of the explanation, but even so, the model might approximate the variation in the density of states. Because of uncertainty in the assumptions, the introduction of further levels to account for the deviation above 100 K has not been attempted.

Since it is well known that Schottky-like heat capacity contributions occur also as differences between Debye and/or Einstein functions with different characteristic temperature, the metallic nature of $CoTe_2(m)$ might give rise to a lower characteristic temperature than that for $FeTe_2$ and a more rapid heat capacity rise will then be expected at intermediate temperatures. This alternative interpretation of the excess heat capacity is also illustrated in Fig. 2, assuming (constant) Debye temperature of 300 K for $FeTe_2$ and 250 K for $CoTe_2(m)$.

Interestingly, the estimated value for the entropy calculated through the cationic and anionic entropy contributions [1] for solid transition-metal chalcogenides is 24.0 cal_{th} mol^{-1} K^{-1} at 298.15 K, or about 3.4 cal_{th} mol^{-1} K^{-1} lower than that observed. This result is analogous to those for other cobalt and nickel chalcogenides as a consequence of the neglect of the contributions from population of low-lying electronic states or bands, which we thus far had been unable to evaluate properly.

The heat capacity increase for $CoTe_2$ above 300 K follows a different pattern from that observed for $FeTe_2$. [26,27] An unusual increase is observed of a temperature as low as 400 K in the latter, probably occasioned by defect formation as in $FeSe_2$, [28] while for $CoTe_2(m)$ only a gradual increase in heat capacity, primarily due to the dilational term is observed up to 900 K. Above this temperature a sigmoid increase is noted from about 23 cal_{th} mol^{-1} K^{-1} at 930 K to about 33 cal_{th} mol^{-1} K^{-1} at 1030 K. This reflects the precipitation of the $Co_{1-x}Te$-phase from stoichiometric $CoTe_2$ as the peritectic decomposition temperature for the $CoTe_2(m)$-phase is approached.

The entropy of $CoTe_2(m)$, the entropies of the elements [29], and the enthalpy of formation of $CoTe_2(m)$ (found by solution calorimetry) [30], have been determined and their

values for $CoTe_2(m)$ at 298.15 K are:

$\Delta_f H^0$, $kcal_{th}\ mol^{-1}$	-17.44 ± 0.7
$\Delta_f S^0$, $cal_{th}\ mol^{-1}\ K^{-1}$	-4.37 ± 0.3
$\Delta_f G^0$, $kcal_{th}\ mol^{-1}$	-16.1 ± 0.8

The latter two values are at variance with those determined by Komarek et al.[30] from decomposition pressures.

Measurements on $CoSe_2$ have thus far revealed only a simple approximately sigmoid heat capacity over both low- and high-temperature regions[31].

VI. THERMOPHYSICAL PROPERTIES OF $FeSb_2$

Let us consider $FeSb_2$ as one example—not necessarily totally typical—of the problems encountered in this endeavour. Electrical and magnetic measurements on well-characterized samples of $FeSb_2$ by Fan et al.[32] led them to conclude that $FeSb_2$ is a semiconductor or a semimetal with an extremely narrow band gap. Further support was provided by the study of the Mössbauer effect from 6.4 to 560 K by Steger and Kostiner[33] who fitted their data to a function indicating that the temperature dependence of the quadrupole splitting is the result of an electrical process which involves the thermal population of an empty conduction band. Hence, the study of the heat capacity of $FeSb_2$ would offer conclusive evidence for the absence of cooperative phenomena in the compound, and also show the effect of band population.

The heat capacity of $FeSb_2$ increases quite monotonically over the entire temperature region and with little evidence of preperitectic decomposition[34]. This contrasts with the X-ray diffraction results by Fan et al.[32] that $FeSb_2$ decomposes into FeSb and Sb under vacuum at 573 K. The decomposition found here (1021.2 ± 0.2) K is in complete agreement with that found by Geiderikh et al.[35] (1021 K) while the results of Kurnakov and Konstantinov[36] (1001 ± 2 K) and Holseth[37] (1004.6 ± 0.5) K are considerably in error.

No trace of the antiferromagnetic transition claimed to exist around 800 K to 1000 K by Rosenqvist[38] and by Holseth and Kjekshus[39] was detected, which accords with the observation by the latter authors that no purely magnetic reflections were obtained in their neutron-diffraction study of $FeSb_2$ around 300 K. Thus, iron is accordingly in a non-magnetic ground state, which presumably arises from the $3d^4$ configuration. The ΔH_d for the peritectic decomposition at 1021.2 K is ($12\,910 \pm 30$) $cal_{th}\ mol^{-1}$.

However, the heat capacity of $FeSb_2$ does not show the pronounced increase at higher temperatures characteristic of $FeTe_2$[26,27] (see Fig. 2). Similar behaviour in $FeSe_2$ has been attributed to defect formation[28], while neither isostructural FeS_2[10] nor isoelectronic $NiSb_2$[40] show comparable excess heat capacities in the higher-temperature region. A comparison of $FeSb_2$ and $FeTe_2$[41] has already been made.

In the Goodenough[42] and the Fan et al.[32] model the $3d$-electron b-band is filled with four electrons, while the next doubly degenerate $a_\parallel$-band is empty. Steger and Kostiner[33] concluded from the unusual temperature dependence of the Mössbauer quadrupole splitting that electrons were promoted across an energy gap of only (33 ± 1) meV (or 265 cm^{-1}), that is, having approximately the same value as that derived by Fan et al.[32] from electrical conductivity measurements ($\sim$210 cm^{-1}). If the band is assumed to be narrow and its population approximated by a Boltzmann distribution, we find that excitation from a fourfold-degenerate b-band does not produce the observed increase in heat capacity. Thus, either the b-band might be split, or further levels or bands in addition to $a_\parallel$ and σ^* are also being populated. We are not at this time able to make a decision between the various alternatives, but should like to remark that a surprisingly good agreement is obtained (see Fig. 3) if a split $(2)b$-band is succeeded by $(2)a_\parallel$ and $(4)\sigma^*$ (in Goodenough's model) with $E_1/hc = 200\ cm^{-1}$ and $E_2/hc = 500\ cm^{-1}$.

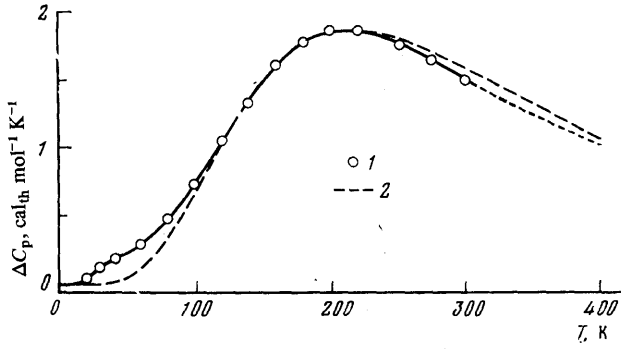


Figure 3. o, Excess molar heat capacity of $FeSb_2$ relative to that of $FeTe_2$. – – –, Calculated Schottky heat capacity for $E_1/hc = 300\ cm^{-1}$, $E_2/hc = 500\ cm^{-1}$, and $g_0, g_1, g_2 = 1, 1, 2$.

VII. CHROMIUM DIANTIMONIDE

The magnetic properties of chromium diantimonide with orthorhombic marcasite-type structure[43] show a maximum in susceptibility of $CrSb_2$ around 600 K and indicate the presence of two unpaired spins per chromium atom at high temperatures, and hence of formally quadrivalent chromium in $CrSb_2$. It was mentioned already by Foex and Graff[44] that $CrSb_2$ showed antiferromagnetic behaviour just as does CrSb, but no evidence was presented. In a later susceptibility study by Holseth and Kjekshus[39] the unusual susceptibility behaviour was confirmed and it was suggested that $CrSb_2$ might be antiferromagnetic with a Néel temperature close to the decomposition temperature. But Adachi et al.[45] interpreted their susceptibility measurements over the range 77 to 900 K in terms of the excitation of electrons from a singlet-to a triplet-spin state with an energy separation of 0.07 eV. The same value of the energy gap was derived from low-temperature resistivity measurements. Accordingly, a broad, Schottky-type heat-capacity maximum of 2.03 $cal_{th}\ mol^{-1}\ K^{-1}$ at 288 K was expected. Adachi et al.[45] carried out heat capacity measurements only above 330 K and the results failed to confirm the correctness of their model.

In view of possible antiferromagnetic spin ordering, Adachi et al.[45] carried out neutron diffraction experiments near 300 K, but did not observe any magnetic reflections. Similar experiments by Holseth et al.[46] showed antiferromagnetic ordering at 4.2 K with doubled cell dimensions in the b- and c-directions. The magnetic spin quantum number is 0.97 per chromium atom and the magnetic moments are coupled parallel in each 011 plane of the magnetic unit cell, but in opposite directions in adjacent planes and with

orientation approximately normal to the 101 plane. Interestingly—of all the compounds with marcasite-type structure—$CrSb_2$ is the only one which shows clear evidence of magnetic ordering. In view of the observed cooperative ordering, a study of the heat capacity behaviour of $CrSb_2$ in the critical region seemed especially interesting. In addition, the increase in magnetic susceptibility to a maximum value around 600 K should also be reflected in the heat capacity and not result in a linear temperature relationship of the kind reported by Adachi et al.[45]

From the randomization of the spins of the two unpaired electrons revealed by magnetic susceptibility and neutron diffraction (neglecting further contributions from orbital states), a magnetic entropy $S_m = R \ln 3 = 2.17$ cal_{th} mol^{-1} K^{-1} is obtained, since the heat capacity of $CrSb_2$ (shown in Fig. 4) shows a small, sharp λ-type transition with a maximum at 274.1 K, where the change from the antiferromagnetic to the paramagnetic state occurs on heating[47].

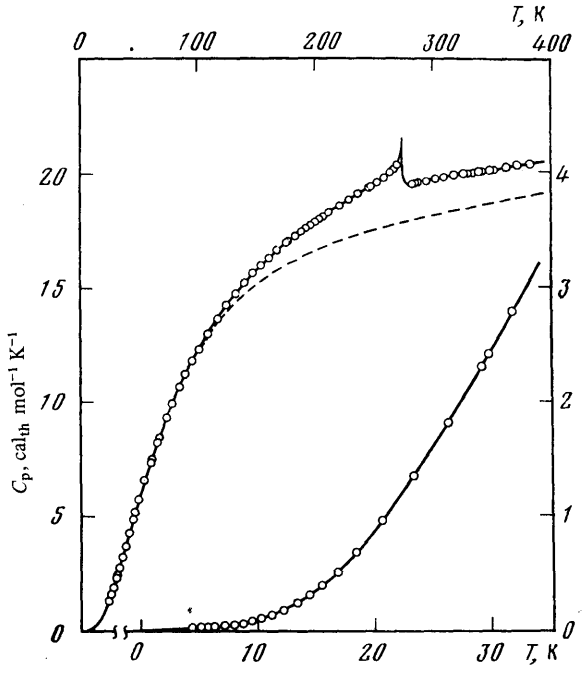


Figure 4. Heat capacity and antiferroelectric anomaly in $CrSb_2$; – – –, the estimated lattice contribution[47].

Obviously, only a fraction of this entropy (0.12 cal_{th} mol^{-1} K^{-1}) is generated in the clearly cooperative part of the transition. The heat capacity of $CrSb_2$ is, however, seen to be unusually high over a wide range in temperature above the transition at 274.1 K. This is evident by comparing it with those of the isostructural analogues $FeTe_2$,[41] $CoTe_2$,[48] and $FeSb_2$;[34] none of these are especially suited as "lattice heat-capacity models"—as they apparently differ substantially in vibrational properties, and the last two are also influenced by conduction-electron contributions. We, therefore, derive the lattice heat capacity of $CrSb_2$ from an estimate of its effective Debye temperature and by the application of a dilational heat-capacity term according to Nernst and Lindemann[49].

The constant Debye temperature used for calculating C_V(lattice) in the higher-temperature region was taken as the maximum of Θ_D in the lower-temperature region, $\Theta_D = 298$ K being obtained at 90 K. The dilational heat capacity is

$$C(d) = C_p - C_v = AC_p^2(T/T_m)$$

where the constant $A = 0.00713$ K mol cal_{th}^{-1} according to Nernst and Lindemann and $T_m = 991.3$ K is the peritectic decomposition temperature found here. Accordingly, the excess magnetic heat capacities are 1.7, 1.6, and 1.1 cal_{th} K^{-1} mol^{-1} at 300, 500, and 700 K respectively. Although this excess heat capacity was not observed by Adachi et al.[45], they nevertheless associated the magnetic behaviour with a transition from a singlet spin ground state to a split triplet state. Accordingly, a Schottky heat-capacity contribution with a maximum 2.03 cal_{th} K^{-1} mol^{-1} at 288 K should be observed.

Even though this model appears to fit the magnetic susceptibility data (disregarding the rather arbitrary subtraction of a temperature independent susceptibility term), it is not in agreement with the neutron-diffraction results, which point to the existence of two unpaired electrons per chromium atom in the ground state. According to our estimate, the total magnetic entropy up to 900 K is about 2.6 cal_{th} mol^{-1} K^{-1} or, well above this temperature, $R \ln 3 = 2.17$ cal_{th} mol^{-1} K^{-1}. In the search for further magnetic contributions the orbital components ought to be considered; according to ligand field theory the ground term of the d^2-configuration in an octahedral field is $^3T_{1g}$ with a total degeneracy $3 \times 3 = 9$. The exact splittings of the ground term are not known and in the zeroth approximation we assume that the first excited state (connected with the disappearance of cooperative magnetism) is a doublet, and that this state is followed by the remaining states, which might roughly correspond to a 3 : 6 Schottky heat-capacity contribution. Further consideration of this resolution is clearly a desideratum. Another point of interest concerns the composition of the $CrSb_2$ phase, but the original paper[47] will need to be consulted for that information.

VIII. CHROMIUM MONOARSENIDE

The heat capacity of chromium arsenide provides an interesting example of these AB compounds[48]. Here the heat capacity shows a distinct bell-shaped transition with a peak at 259.9 K related to the disappearance of antiferromagnetic helical ordering on heating. The entropy of this transition is 0.69 cal_{th} mol^{-1} K^{-1}. At 1170 K another transition is observed related to the phase change from the (300 K, stable) MnP-type to the NiAs-type structure. The entropy of the latter (gradual) transition is 0.077 cal_{th} mol^{-1} K^{-1}.

Chromium monoarsenide has been extensively studied by X-ray and neutron-diffraction, magnetic-susceptibility, and magnetization techniques, and two solid-state transitions have been described. The thermodynamic properties of CrAs are largely unknown, however, except for the heat capacity measurements by Kazama and Watanabe[50] in the region from 180 to 280 K. Our investigation was undertaken to improve and extend the earlier heat capacity data, thereby providing thermodynamic data for CrAs over the stability ranges of the solid phases, and, in particular,

to explore the detailed trends in the regions of both the low-temperature transformation and higher-temperature transition.

According to Haraldsen and Nygaard[51], the magnetic susceptibility of CrAs increases steadily over the region from 80 to 600 K, indicating an enhanced population of higher magnetic states. Yuzuri[52] found a peak in the susceptibility at 820 K which was taken to imply an antiferromagnetic to paramagnetic transition in this region, while Selte and Kjekshus[53] observed a further small increase in susceptibility in the region from 800 to 970 K. Above 300 K, one might then expect to encounter an excess heat capacity due to the population of excited electronic states in chromium and also a thermal effect accompanying the transformation of the MnP-type into the NiAs-type structure.

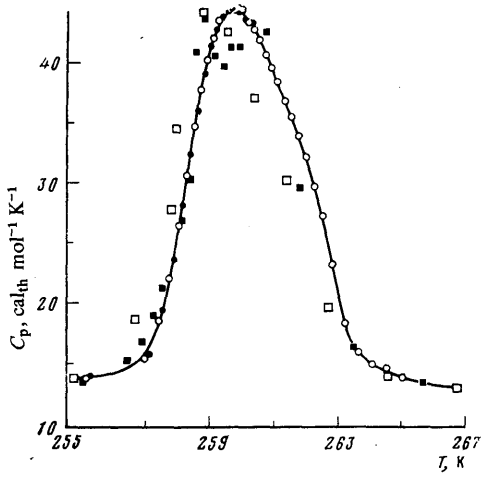


Figure 5. Heat capacity anomaly associated with double helical-spin ordering in $CrAs_2$.[48]

Below 300 K, a sudden structural change occurs in CrAs, which is related to a double helical-spin ordering with spiral propagation in the AB-plane. Watanabe et al.[54,55] reported that this occurred at about 280 K, while discontinuities in the lattice constants and anomalies in electrical resistivity and thermoelectric power occurred at 265 K. Selte et al.[56,57] observed the transition to go to completion at 272 K on heating, while the spiral structure reappeared at 261 K on cooling. According to Boller and Kallel[58], the transformation takes place in the range from 190 to 240 K and shows hysteresis and supercooling effects. The volume contraction on heating is accompanied by a shortening of the distance of one additional Cr-Cr contact considerably below the value r_C = 318 pm, which, according to Mott[59,60] and Goodenough[42], is the critical intermetallic distance for the localized-collective electron behaviour.

The heat capacity at the low-temperature transition is shown in Fig. 5. It rises to a rounded peak and then drops gradually with a shoulder on the high-temperature side. A cooling curve recorded at a rate of about 0.09 K min^{-1} shows that the sample does supercool by at least 6 K, as might be expected for a first-order transition.

In attempting to ascertain the thermodynamics of the magnetic ordering transition, we note that apparently none of the MnP-type pnictides is diamagnetic[61]. This makes it difficult to find an adequate lattice heat-capacity model among the isostructural analogues of CrAs, such as FeAs, CoAs, MnAs, and FeP. A further complication is that Schottky-type contributions to the heat capacity are anticipated above the transition. In order to estimate the lattice contribution, the heat capacity curve far below T_{tr} was connected smoothly to the C_p curve above the transition. The estimated lattice heat capacity is represented in Fig. 5 by a dashed line. With this lattice estimate, we find ΔS_{tr} = 0.69 cal_{th} mol^{-1} K^{-1} and ΔH_{tr} = 177 cal_{th} mol^{-1}. Watanabe et al.[54] report T_{tr} = 265 K and ΔH_{tr} = 124 cal_{th} mol^{-1} for this transition, determined by continuous heating adiabatic calorimeter. Despite the large differences in T_{tr} and ΔH_{tr} compared with our study, they report a shape of the transition curve that is quite similar to ours. The discrepancies in T_{tr} and ΔH_{tr} might be partly explained by the different methods used: dynamic versus equilibrium measurements—and differences in the lattice heat capacity, but probably differences in the nature nature of the samples are more important.

The value of the Néel temperature, T_{tr} = (259.86 ± 0.05) K, is not within the broad temperature range from 240 to 190 K assigned to the occurrence of the transition by Boller and Kallel[58] and is also much lower than the approximate value of 280 K reported by Watanabe et al.[54] from neutron diffraction studies.

Crystallographic and magnetization studies[58] have shown that the transition is of first order. The shape of the curve suggests that the order is higher but the hysteresis and long equilibrium times support the hypotheses of a first-order transition. Bean and Rodbell[62] presented a model for first-order magnetic transitions, in which the transition is shifted to higher temperatures as a consequence of the dependence of exchange interactions on interatomic distances and the volume change on transition.

IX. ACTINIDE PNICTIDES

U_3Pn_4 compositions. Attention has been drawn increasingly to the magnetic and thermophysical properties of uranium pnictides (U_3Pn_4) (in which Pn = P, As, Sb, or Bi), all of which have cubic Th_3P_4 structures. Magnetic susceptibility and magnetization measurements show that all of them are ordered to a ferromagnetic state below 300 K and that the Curie-Weiss law is obeyed above the Curie temperature (T_C) up to at least 400 K. The paramagnetic moment increases with increasing pnigogen size, but lack of such a correlation for the ordering temperature might indicate that the magnetic coupling is anomalously weak in U_3Pn_4.

For U_3X_4, the U^{4+} site has S_4-symmetry, which splits the ninefold degenerate $^3H_4$ ground term into five singlets and two doublets. Troc et al.[63] calculated the energy levels of the ground term using a point charge model and obtained a good correlation with their high-temperature magnetic susceptibility data. The lowest excited level, a singlet, is 9 cm^{-1} above the singlet ground level, and is followed by seven higher levels (the lowest of which is at 700 cm^{-1}).

So far we have only examined uranium arsenide and antimonide[64]; for the bismuthide and for the resolution of the problem of the low-temperature heat-capacity data for U_3P_4 reported by two authors—who disagree by a factor of two (!) as regards the entropy of transition—more work

is contemplated. Moreover, we need to study the heat capacities of the isostructural diamagnetic thorium analogues to be assured to a good resolution of the magnetic heat capacity.

Single crystals of U_3As_4 [64] are semimetallic with a resistivity of 290 pohm cm^{-1} at 300 K, while U_3Sb_4 is reported to be metallic [65]. Our electronic contributions are consistent with these interpretations.

It is well known that the magnetic contribution to the heat capacity cannot be easily separated from the total heat capacity [66]. Lacking heat-capacity data for diamagnetic Th_3As_4 and Th_3Sb_4, our estimate of ΔS_{tr} is somewhat arbitrary. Stalinski et al. [67] used the Heisenberg theory of spin-wave interactions [68] to estimate the magnetic heat capacity below $T_C/2$ for U_3P_4. We also used this method to establish the Debye-temperature curve at low temperatures, but, as pointed out by de Jongh and Miedema [69], this method can only be expected to be rigorous for insulating ferromagnets. Neutron-diffraction measurements [70,71] favour a non-collinear alignment of the spins and electrical resistivity measurements for U_3P_4 and U_3As_4 show a strong magnon conduction electron scattering [72].

From the adjusted heat capacities below $T_C/2$ and above T_C, the effective Θ_D's for U_3Sb_4 were evaluated and plotted against temperature. The gap in the curve caused by the transition was bridged and converted into a non-cooperative heat capacity. That for U_3As_4 was then calculated by the method of corresponding states [73]. The excess (cooperative) heat capacities were obtained by the subtraction of the respective integrated curves. Cooperative entropy values of 4.15 cal_{th} mol^{-1} K^{-1} for U_3As_4 and 6.60 cal_{th} mol^{-1} K^{-1} for U_3Sb_4 were thus obtained.

Since at the transition temperature essentially only the two lowest singlets are populated, an effective spin (s) equal to 1/2 results. This gives a $\Delta S_{tr} = R \ln(2s + 1) = R \ln 2 = 1.38\,cal_{th}$ (mol U)$^{-1}$ K^{-1}, [74] in good agreement with the experimental value for U_3As_4: ΔS_{tr} = 1.4 cal_{th} (mol U)$^{-1}$ K^{-1}. The ΔS_{tr} for U_3Sb_4 (2.2 cal_{th} mol^{-1} K^{-1}) cannot be explained thus unless the higher excited levels are lower in energy than those for U_3P_4. [63] The reputed presence of conduction electrons in U_3Sb_4, however, has been neglected in the above model.

Since these ΔS_{tr}'s are so much smaller than theoretical values of $\Delta S_{tr} = R \ln(2J + 1) = R \ln 9$ for the $^3H_4$ ground term and since the observed heat capacities at high temperatures are seen to be much larger than would be expected from lattice dilational contributions, additional electronic contributions are to be anticipated.

The lattice heat capacities of U_3As_4 and U_3Sb_4 at constant volume were generated from effective Θ_D values equal to 240 and 190 K, obtained as the maximum values of the adjusted heat capacities below the transition. A dilational contribution $C(d) = C_p - C_v$ was calculated from the Nernst-Lindemann expression $C(d) = AC_p^2(\frac{T}{T_m})$, in which A = 0.0212 K mol cal^{-1} and T_m, the melting point of the compounds, is taken to be 1700 K. The quantity $[C_v + C(d)]$ is then subtracted from the observed heat capacity to give the total electronic heat capacity, as shown in Fig. 6. This arises from the cooperative (magnetic) contribution already discussed and the excitation of additional electronic levels. Assuming the energy levels of U_3Sb_4 to be approximately the same as those for U_3P_4, the Schottky heat capacity contribution in the region above T_C can be calculated from the levels and degeneracies given by Troc et al. [63], assuming that the two low levels represent a doubly degenerate level responsible for the cooperative phenomenon. The resulting neat capacity, shown in Fig. 6, is essentially compatible with the high-temperature data, but a better fit may be obtained by lowering some energy values slightly.

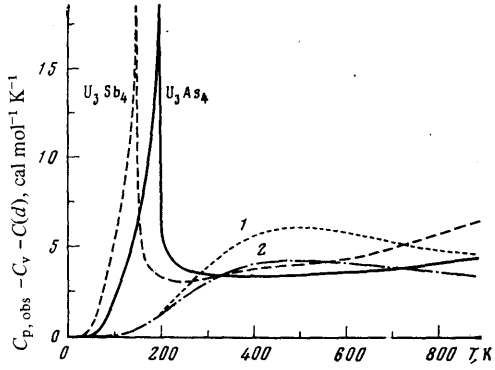


Figure 6. Excess heat capacities $[C_{p,obs} - C_v - C(d)]$ for ferromagnetic transitions in U_3As_4 and U_3Sb_4. The higher-temperature data are fit by a two level Schottky heat capacity contribution using the energies of Troc et al. (– – – – –) [63] and those of the authors (cf. text) (–·–·–). [64]

Entropies of transition significantly below the value expected for the ground-term degeneracy are observed for several uranium compounds [66]. As pointed out by Counsell et al. [75], such low ΔS_{tr} values are evidence of crystal-field effects.

A model that does not require assumptions about a definite ionic state and allows for the essential interdependence of magnetic and conduction phenomena has been proposed by Robinson and Erdös [76]. The model takes into account the closeness of the 5f- and the 6s-levels of uranium. This model has been successful in explaining the electronic and magnetic transition in UP. The larger ΔS_{tr} for U_3Sb_4 can be explained qualitatively by the fact that U_3Sb_4 is more metallic and has a lower ordering temperature than U_3As_4. This model cannot be applied to U_3As_4, since its resistivity behaviour is very different from that of uranium monopnictides.

UPn$_2$ compositions. The UPn$_2$ compositions we have studied are again the arsenide and the antimonide only. These results [77] already published in a concise form will be but briefly mentioned here.

In the dipnictide series UN_2 is an exception; it is stable only under high N_2 pressure and has the fluorite structure [78]. The remaining members UP_2, UAs_2, USb_2, and UBi_2—are isostructural with the tetragonal Cu_2Sb structure. Magnetic susceptibility and neutron diffraction measurements have been made on the four dipnictides from UP_2 to UBi_2. The dependence of the inverse magnetic susceptibility on temperature indicates that all the compounds are ordered antiferromagnetically and that Curie-Weiss behaviour obtains above the ordering (Néel) temperature. The paramagnetic moment increases monotonically with increasing pnigogen size, but Néel temperatures do not. Hence the magnetic coupling may either be anomalously weak, as in UP_2 or anomalously strong, as in UAs_2.

The antiferromagnetic structures of UP_2, UAs_2, and USb_2 determined by neutron diffraction (in the ordered state) consist of ferromagnetic sheets of uranium ions stacked perpendicularly to the c-axis and in the sequence $+ - +$. The magnetic unit cell is twice as large as the chemical one due to its doubled c-axis. In contrast to this, the UBi_2 chemical and magnetic unit cells are identical and the ferromagnetic sheets have the order $+ - + -$. The compounds display metallic conduction with $\rho(298\,K) = 1.83 \times 10^{-4}$ and 1.95×10^{-4} ohm cm for single-crystal samples of UP_2 and UAs_2 respectively [79].

The heat capacity of UP_2 (22.5 to 350 K) has been reported by Stalinski et al. [80] Here a prominent lambda anomaly at 203.2 K accords well with the transition to the antiferromagnetic state, as observed in magnetic susceptibility measurements. In our measurements on UAs_2 and USb_2, [81] we found that both substances show λ-type transitions in the heat capacity with maxima at 272.2 and 202.5 K respectively. Heat capacities below 5 K were extrapolated with a term proportional to T^3 (Debye lattice contribution) and one proportional to T (conduction electron contribution γ). The respective parameters, the Θ_D and γ, were taken from C_p/T versus T^2 plots of the heat capacity below about 20 K. The values of γ were found to be 1.36×10^{-3} cal_{th} mol^{-1} K^{-2} for UAs_2 and USb_2.

Difficulties associated with determination of magnetic heat capacity contributions have been alluded to already and are encountered with uranium compounds involving Group IV, V, and VI elements [66,75]. In the absence of heat-capacity data for the isostructural diamagnetic compounds (i.e. the corresponding thorium compounds) such resolutions must be regarded as tentative and probably too low. It is interesting to note, however, that the heat capacity of USe_2 [82] (with nearly the same molecular weight as UAs_2 although its crystal structure differs) agrees rather well with the heat capacity of the latter compound for some ranges both above and below the transition and with our lattice contribution described below.

The magnetic ordering contributions were determined by plotting the effective Θ_D's for the total heat capacities as a function of T and by interpolating over the gap caused by the enhanced heat capacity in the transition region. The Θ_D's thus obtained over this interval were used to generate "lattice" heat capacities, which were then integrated.

The amount of entropy to be expected is relevant to the interpretation of the ΔS_m, despite reservations about well defined oxidation states for conducting compounds involving the pnigogens. Naively, one may—at least initially—adopt a model with a specified oxidation state for uranium (U^{4+}) and proceed from the free-ion, ground term ($^3H_4$), on the assumption of Russell-Saunders coupling, to the expected magnetic entropy $R \ln(2J + 1) = 4.37$ cal_{th} mol^{-1} K^{-1}. The failure of the experimental results to account for this amount of entropy is usually attributed to the crystal-field quenching of the orbital moment. Occasionally the paramagnetic moment and the excess entropy in such systems can be identified more closely with spin-only values, which in the present case would be $R \ln(2S + 1) = R \ln 3 = 2.18$ cal_{th} mol^{-1} K^{-1}. The paramagnetic moments are all less than the free-ion values (3.58 μ_B) and vary from below the spin-only value (2.83 μ_B) for UP_2 to near the free-ion value for UBi_2. However, $\Delta S_m(UAs_2) = 0.99$ cal_{th} mol^{-1} K^{-1} and $\Delta S_m(USb_2) = 1.70$ cal_{th} mol^{-1} K^{-1} are both well below even the spin-only values.

The UP_2 heat capacity near 350 K is already well above the Dulong and Petit limit and the trend of these data contrasts markedly with that for UAs_2 and USb_2. Magnetic susceptibility [83], electrical conductivity [84], and more recently X-ray crystallographic [85,86] studies have shown the presence of a phase transition in UP_2 near 356 K, where the tetragonal superstructure disappears on heating.

X. THE COPPER–SULPHUR SYSTEM

Although early investigations indicated that the copper–sulphur system is relatively uncomplicated and consists, in fact, of only three binary phases, covellite (CuS), digenite ($Cu_{1.80}S$), and chalcocite (Cu_2S), recent studies have produced a veritable population explosion of distinct new phases in the system, which have not as yet yielded an unambiguous phase diagram, particularly in the region below 400 K. The marked ambiguity is produced by a multiplicity of phases, a strong tendency of the copper–sulphur system to exhibit metastability, and confusion—partly because of the similarity—of the X-ray diffraction patterns and optical properties. Moreover, extensive solid solutions, unquenchable phases, and phase transformations produced by grinding and handling have created considerable confusion since the comprehensive study of the phase equilibria in this system by Roseboom [87]. Since this almost classical study, numerous additional papers have appeared reporting the application of a great variety of techniques. Perhaps one of the most interesting, from the point of view of a thermodynamicist, is one as yet not in print, by R. W. Potter [88], in which he has been able to resolve much of the contradictory nature of the other data by means of galvanic cell measurements to delineate the metastable equilibria, the stable phase diagram, and the thermochemical properties of both phases.

We may note that, like the first system mentioned in this paper, the present one, the last to be discussed, is mineralogical. However, marcasite is already known in the literature, whereas our data on the copper–sulphur system are the least complete of any that I have discussed today and work is still, therefore, in very active progress. We are eager to obtain thermophysical data to test the correctness of Potter's galvanic cell studies [88].

To date, we have studied the high- and low-temperature heat capacities of the three copper compositions which I mentioned as those originally identified with the system. We are undertaking measurements at the present time on anilite and djurleite.

One of the remarkable aspects of the behaviour of these materials is in the fact that, under some temperature conditions, many of them show "superionic conductivity" to an interesting degree.

Turning our attention to digenite, we note first of all that at about 350 K high-temperature digenite transforms on cooling into low-temperature digenite. Rather more amazing is the fact that at 310.8 K—just above room temperature—a transition occurs which we are obliged to describe as a disproportionation transition. Apparently, on cooling to about this temperature, one departs from the solid-solution range of the low-temperature digenite phase and crosses the boundary into the low-temperature digenite–djurleite field. In other words, the low-temperature digenite disproportionates to some extent into djurleite. Although one is inclined to think of disproportionation equilibria as relatively slow phenomena even at elevated temperatures, there is nothing very slow about this transition. It should be noted, of course, by examining the

phase diagram[87,89], that the boundary mentioned above apparently continues to be a function of temperature well below 300 K.

It appears that the transformation takes place gradually as one goes down in temperature and our measurements indicate that it is insufficient to supercool 10 or 20 K below the above transition; one has to go to very low temperatures indeed if a reproducible enthalpy of disproportionation is sought. As a matter of fact, we found it routinely most convenient to cool a full 100 K below the transition in order to ensure a complete transformation. The exact trend of the boundary between the fields is apparently not yet well delineated, but we find that we can reproduce to within approximately 0.01 per cent the enthalpy increment associated with this transition. The overall shape of the transition is presented in Fig. 7. The dashed lines represent an interim estimate of the lattice contribution, which will probably ultimately need revision[90].

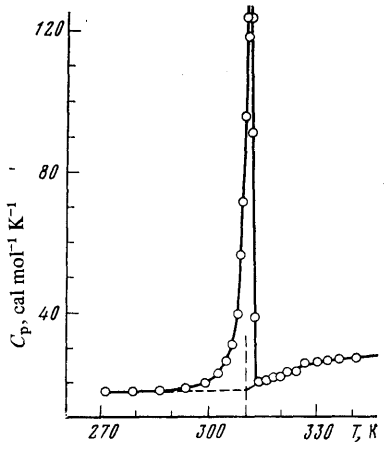


Figure 7. The heat capacity and disproportionation anomaly in lowdigenite $Cu_{1.80}S$.[90]

The enthalpy increment of this transition (ΔH_{tr}) is 477 cal$_{th}$ K^{-1} and the corresponding entropy is 1.50 cal$_{th}$ mol^{-1} K^{-1} or just slightly larger than $R \ln 2 = 1.38$ cal$_{th}$ mol^{-1} K^{-1}. In all respects this has proven to be one of the most striking disproportionation transitions ever encountered in that the rapidity with which equilibrium is reached is unusual. A detailed analysis of the heat-capacity curve below the transition has not yet been completed but it will presumably show excess heat capacity for a gradual transformation of the sample with temperature.

It has been my pleasure to summarize for you some of the recent types of phenomena we have been encountering in the heat-capacity studies in recent months in both the chalcogenides and the pnictides. Were greater time available, more examples could have been discussed and presented and would have shown an even greater diversity. We have not yet reached the point where we recognize anything which can be described as "typical behaviour" and find rather a very interesting variety of phenomena.

There still remains a great deal more of "systematic" work to be done. Table 2 does summarize the thermophysical functions which have become available as a result of our studies on the compounds mentioned in this presentation.

Table 2. Thermodynamic functions for chalcogenides and pnictides at 298.15 K recently determined by Grønvold and Westrum et al.

Substance	S°, cal mol^{-1} K^{-1}	$H^\circ - H^\circ_0$, cal mol^{-1}	$-[(G^\circ - H^\circ_0)/T]$ cal mol^{-1} K^{-1}
Chalcogenides			
FeS_2 (marcasite)	12.88	2328	5.07
$CoSe_2$	23.10	3543	11.21
$CoTe_2$	27.37	3889	14.32
CuS	—	—	—
$Cu_{1.80}S$	—	—	—
Cu_2S	—	—	—
Pnictides			
$FeSb_2$	25.98	3905	12.88
$CrSb_2$	27.46	4009	14.01
CrAs	15.40	2506	6.99
UAs_2	29.41	4282	15.05
U_3As_2	73.87	10405	38.97
USb_2	33.81	4596	18.39
U_3Sb_4	83.60	10943	46.89

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Infrared Spectroscopy of the Hydrogen Bond as a Method for the Investigation of Intramolecular Interactions

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Infrared spectroscopic data on hydrogen-bonded complexes incorporating the main classes of organic and organoelemental electron donors and electron acceptors are examined and surveyed. The dependence of the parameter $\Delta\nu$ (the frequency shift of the stretching vibration of the A-H bond in the infrared spectrum of the electron acceptor on formation of the hydrogen-bonded complex) on intramolecular interactions in the molecules of the species involved in the hydrogen bond is analysed. The use of this parameter in the investigation of weak electronic effects of substituents in the molecules of electron donors and electron acceptors involved in the formation of the hydrogen bond is considered.
The bibliography includes 191 references.

CONTENTS

I. Introduction 1198
II. Intramolecular interactions in electron donors involved in hydrogen-bonded complexes 1199
III. Intramolecular interactions in electron acceptors involved in hydrogen-bonded complexes 1206

INTRODUCTION

There has been a continuous increase in the number of reports surveying the extensive experimental data on complexes with an intermolecular hydrogen bond; these surveys help to create a modern theory of the hydrogen bond (see, for example, Refs. 1–6). At present the state of the theory is such that it permits a semiempirical (for example, on the basis of spectroscopic manifestations of the hydrogen bond) investigation of the fine details of the molecular structure of the electron acceptor A–H and the electron donor B, forming a hydrogen-bonded complex of the type A–H...B. One of the main criteria of the existence of the hydrogen bond is the shift $\Delta\nu$ of the stretching vibration frequency ν(A–H) of the electron acceptor on formation of the hydrogen bond, which can be readily measured experimentally in the infrared spectrum. The shifts $\Delta\nu$ yields important information about the structure of the electron donor and electron acceptor and particularly about the intramolecular interactions in these molecules; however, so far this information has been inadequately surveyed and analysed.

The influence of intramolecular interactions in electron donor and electron acceptor molecules on their ability to form hydrogen-bonded complexes is analysed in the present review. Among the extensive literature data, we discuss almost exclusively those obtained in the analysis of $\Delta\nu$ in infrared spectra, since these quantities are known for the majority of the hydrogen-bonded complexes investigated. Mainly studies undertaken to obtain information on the basis of the $\Delta\nu$ about the electronic structure of the species involved in the hydrogen bond (i.e. the electron donor and electron acceptor) are considered.

We shall consider briefly the validity of using the parameter $\Delta\nu$ for the solution of the problem formulated. The hypothesis[7,8] of a linear relation between $\Delta\nu$ and the enthalpy of formation of the hydrogen bond ΔH has been confirmed[9–12] only for short series of compounds. For a large number of hydrogen-bonded complexes of the type phenol (and probably any other electron acceptor) – electron donor, a quadratic relation $\Delta\nu \propto (\Delta H)^2$ is observed[3]. A relation of the type $(\Delta H)^2 = 0.11\,(\Delta\nu - 40)$ describes satisfactorily the variation of ΔH with $\Delta\nu$ over the entire known range of the energies of phenol hydrogen bonds[3], i.e. it is valid for both strong and weak hydrogen bonds. However, this relation must be used with a certain amount of caution, because it is empirical and will therefore be inevitably revised in the future as more accurate values of ΔH become available for weak hydrogen bonds. However, for the weakest hydrogen bonds $\Delta\nu$ values not only characterise the hydrogen bond but also reflect the influence of non-specific interactions in solution (for example, van der Waals interactions). However, within the limits of each of the narrow series of compounds (derivatives of benzene, ethylene, etc.) and under standard experimental conditions (constant electron acceptor, solvent, experimental temperature, and concentration, which is the case in virtually all the studies considered in this review), the influence of non-specific interactions on $\Delta\nu$ can be assumed constant to a first approximation for all the representatives of the given narrow series. The main task of the present review is a survey of the studies of intramolecular interactions in the above narrow series of electron donors on the basis of the analysis of the changes in the parameter $\Delta\nu$ in these series.

An important generalisation described in the literature is the "rule of the product of factors"[4,5], which characterises quantitatively the contributions of the electron donor and electron acceptor to the enthalpy of the hydrogen bond and, in the absence of strong steric hindrance, also in general to the capacity of the electron donor and electron acceptor for the formation of any intermolecular hydrogen-bonded complexes. This rule is characteristic of both the donor–acceptor interaction as a whole and of its special case — hydrogen bonding. It is known (see, for example, Gur'yanova et al.[13]) that the enthalpy of complex formation depends significantly on the electron densities at the donor and acceptor centres, which are in their turn determined by the intramolecular interactions (the inductive and mesomeric effects) in the donor and acceptor molecules. The influence of these effects is characterised quantitatively by the substituent constants of the Taft–Hammett type[14].

It follows that for hydrogen-bonded complexes there should be a relation between the $\Delta\nu$ and the Taft–Hammett constants of the substituents in the electron donor and electron acceptor molecules. For narrow series of electron donors, this relation should be linear. The influence of steric factors on the formation of the hydrogen bond can be estimated by methods of correlation analysis.

The great sensitivity of the parameters $\Delta\nu$ to molecular structure factors makes it possible to investigate fine details in their changes (particularly in series of compounds with related structures).

II. INTRAMOLECULAR INTERACTIONS IN ELECTRON DONORS INVOLVED IN HYDROGEN-BONDED COMPLEXES

Data for the influence of substituents linked to the donor centre, which is responsible to the greatest extent for the electron-donating capacity of the entire molecule in the formation of the hydrogen bond, were arranged systematically in the present review on the basis of the type of donor centre (an element of Group V, VI, or VII, a multiple carbon–carbon bond). Particular attention has been devoted to the consideration of intramolecular interactions in compounds containing elements of the silicon subgroup as substituents in view of the importance of this problem for the chemistry of organoelemental compounds.

1. Electron Donors containing Group V Elements

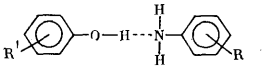
The electron-donating capacity of nitrogen derivatives R_3N varies over a wide range, and together with the inductive effect of R, is determined also by the conjugation effects in the R–N fragments and by the steric factors which control the possibility of the mutual approach of the donor and acceptor centres on formation of the hydrogen bond[10,15–22].

Table 1. The parameters $\Delta\nu$(O–H) (cm^{-1}) for the infrared spectra of certain hydrogen-bonded complexes.

Electron donor	Electron acceptor			References
	C_6H_5OH	p-ClC_6H_4OH	p-FC_6H_4OH	
H_3N	462	—	—	20
C_5H_5N	465	491	489	16
$(C_2H_5)_3N$	556	586	576	16

Table 1 shows that the frequency shift $\Delta\nu$(OH) in the hydrogen-bonded complexes of aliphatic amines and pyridine derivatives depends on the type of electron acceptor employed[16,20,23,24]. The study of hydrogen bonds between methanol and pyridine derivatives[25] showed that the presence of bulky substituents in the 2- and 6-positions in the electron donor molecule hinders the formation of the hydrogen bond. Steric factors have a similar influence both on the electron-donating capacity of pyridine derivatives in the formation of a hydrogen bond and on their basicity. This is indicated by the correlation between the parameter $\Delta\nu$(O–H) for methanol and the pK_a of pyridine derivatives. In the study of hydrogen bonds in cyclic azoles[26,27] it was established that imidazoles have a greater electron-donating capacity than pyrazoles. The electron-donating properties of the "pyridine" nitrogen atoms increase after the introduction of electron-donating substituents into the heterocycle and decrease in the presence of electron-accepting substituents.

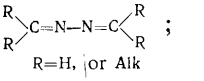
The influence of substituents in the electron donor molecule (substituted aniline) has been estimated quantitatively in relation to the hydrogen-bonded complexes between aniline and phenol derivatives[28]. The values of $\Delta\nu$(O–H) for phenol involved in the formation of a hydrogen-bonded complex of the type



are correlated with the enthalpy of complex formation and with the Hammett σ constants of the substituents R.

Elements of the nitrogen subgroup exhibit different electron-donating capacities in the formation of the hydrogen bond, decreasing in the sequence N ≫ P > As,[29,30] Such variation of the electron-donating capacities is observed also for their aliphatic derivatives. In aromatic compounds the phosphorus atom forms stronger hydrogen bonds than nitrogen[31]. Thus the values of $\Delta\nu$(O–H) for phenol are 800 and 240 cm^{-1} in the presence of $(C_2H_5)_3N$ and $(C_4H_9)_3P$ respectively and at 150 and 240 cm^{-1} in the presence of $(C_6H_5)_3N$ and $(C_6H_5)_3P$ respectively. According to the authors[31], the electron-accepting properties of tervalent phosphorus cannot be explained by the involvement of the d orbitals of the phosphorus atom in the bonding. However, we may note the appreciable discrepancy between $\Delta\nu$(O–H) obtained for triethylamine by the above workers[31] (800 cm^{-1}) and the value measured by Drago and Epley[16] (556 cm^{-1}).

The formation of multiple bonds by the nitrogen atom or its involvement in conjugation alter appreciably the electron-donating properties of compounds containing this atom as a donor centre. Thus in the azines



there may be p,π conjugation of the lone electron pairs of the nitrogen atoms with the π electrons of the neighbouring azomethine linkages[32]. The electron density at the nitrogen atoms, which determines their electron-donating properties, should therefore be determined by the degree of p,π conjugation in addition to the inductive effect of the substituents. The infrared spectra of the hydrogen-bonded complexes of azines with deuterochloroform, potentiometric data, and quantum-mechanical calculations confirmed the existence of p,π conjugation in azines[32].

The study of the electron-donating capacity of the nitriles R–C≡N and isonitriles R–N≡C established that the parameter $\Delta\nu$(OH) for phenol is correlated with the Taft inductive constant σ^* of the substituents R.[33–35] Isonitriles have a greater electron donating capacity compared with nitriles (Table 2). Thus the lone electron pair of the carbon atom in isonitriles $R-\overset{\cdot\cdot}{N}\equiv\overset{\cdot}{C}$ forms a stronger hydrogen bond than the electron pair of the nitrogen atom in nitriles. The deviations of the points corresponding to BrCN and ICN from the correlation straight line for RCN, i.e. $\Delta\nu$(O–H) = 162.7–38.56 σ^*_R, can be accounted for, according to a number of workers[33–35], by the contribution of the resonance structures $X-C\equiv N \leftrightarrow X^+ = C = N^-$. The electron-donating capacity of dimethyl aminobenzonitriles has been investigated[36]. Analysis of the correlations between $\sqrt{\Delta\nu(O-H)}$ (with phenol and methanol as electron acceptors) and the σ constants of the substituents in benzonitriles and between $\sqrt{\Delta\nu(O-H)}$ and the σ^- constants of the substituents in dimethylanilines as well as enthalpy data have shown that the nitrile group is the reaction centre in dimethylaminobenzonitriles.

Alkyl thiocyanates have a smaller electron donating capacity than nitriles[37,38] (Table 2). The values of $\Delta\nu$(O–H) for phenol involved in the formation of hydrogen bonds with alkyl thiocyanates are linearly related to the Taft σ^* constants for the alkyl substituents. On the basis of the decrease of the electron-donating capacity in the sequence nitriles > thiocyanates > isothiocyanates, it has been suggested that the hydrogen bond formed by thiocyanates involves the nitrogen atom, while that formed by isothiocyanates involves the sulphur atom[39]. The reduced electron donating capacity of the thio-derivatives compared with nitriles is associated with the conjugation within the NCS group[39]. The authors of a later study[40] of intermolecular interactions of alkyl isothiocyanates with phenol also concluded that alkyl isothiocyanates have a lower electron-donating capacity than alkyl thiocyanates and nitriles but, in contrast to Barakat et al.[39], they postulate that the hydrogen bonds of isothiocyanates are formed with the participation of the nitrogen atom and not sulphur.

Table 2. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

Electron donor	$\Delta\nu$(O–H), cm^{-1}	References
CH_3CN	159	33
$C_6H_{11}CN$	174	33
C_6H_5CN	153	33
BrCN	102	34
CH_3NC	228	33
$C_6H_{11}NC$	250	33
C_6H_5NC	203	33
CH_3SCN	146	38
C_2H_5SCN	152	38
CH_3NCS	107	40
C_2H_5NCS	113	40

A spectroscopic study of the electron-donating capacity of organosilicon amines showed[41,42] that the $\Delta\nu$(C–D) shift of the stretching frequency of the bond in deuterochloroform in mixtures with silylamines amounts to 50–60 cm^{-1} for compounds of the type $(CH_3)_3SiNHR$, 60–80 cm^{-1} for $(CH_3)_3SiNR_2$, and 30–35 cm^{-1} for the cyclic derivatives $[(CH_3)_3SiNR]_3$. In view of the greater electron-donating capacity of the isostructural carbon derivatives, the authors[41,42] concluded that there is a strong d_π–p_π interaction in the Si–N group (Table 3; compounds 1 and 2, 5 and 6, and 8 and 9). Here and henceforth in the review the d_π–p_π interaction is understood as the manifestation of the π-acceptor properties of the silicon and phosphorus subgroup elements (when these elements are linked to atoms having lone electron pairs or to α,β-unsaturated carbon substituents). Together with the hypothesis of the involvement of the vacant *nd* orbitals of these elements, there exists an alternative view concerning the explanation of the π-acceptor properties[43,44], based on an examination of hypervalent bonds[45]. The electron-donating capacities of two series of compounds, $(CH_3)_3En(CH_3)_2$ and $E[N(CH_3)_2]_4$ (E = C, Si, or Ge), have been estimated for the formation of hydrogen bonds by these derivatives with deuterochloroform[46]. The weakest hydrogen bonds are formed by silicon derivatives owing to the delocalisation of the *p* electrons of the nitrogen atom over the vacant *d* orbitals of the silicon atom (the effect of the d_π–p_π interaction). On passing to germanium derivatives the effect of the d_π–p_π interaction is appreciably weakened (Table 3; compounds 2 and 3, 6 and 7, and 9 and 10, and 11 and 12).

Table 3. The parameters $\Delta\nu$(C–D) for the infrared spectra of hydrogen-bonded complexes (with deuterochloroform as the electron acceptor).

No.	Electron donor	$\Delta\nu$(C–D), cm^{-1}	References
1	$(CH_3)_2CNHC_2H_5$	89	41
2	$(CH_3)_2SiN(C_2H_5)_2$	64	42
3	$(CH_3)_3GeN(C_2H_5)_2$	82	42
4	$(CH_3)_3SnN(C_2H_5)_2$	90	42
5	$(C_2H_5)_3N$	91	49
6	$(C_2H_5)_2SiN(CH_3)_2$	51	49
7	$(C_2H_5)_3GeN(CH_3)_2$	81	50
8	$(CH_3)_2CN(CH_3)_2$	96	46
9	$(CH_3)_3SiN(CH_3)_2$	61	46
10	$(CH_3)_3GeN(CH_3)_2$	76	46
11	$[(CH_3)_2SiNCH_3)_3$	36	48
12	$[(C_2H_5)_2GeNCH_3]_3$	77	48

Table 4. The parameters $\Delta\nu$(C–D) for the infrared spectra of hydrogen-bonded complexes (with deuterochloroform as the electron acceptor).

No.	Electron donor	$\Delta\nu$(C–D), cm^{-1}	References
1	$(C_2H_5)_2SiNC_5H_{10}$	15	54
2	$(C_2H_5)_2SiCH_2NC_5H_{10}$	60	54
3	$(C_2H_5)_2Si(CH_2)_2NC_5H_{10}$	80	54
4	$(C_2H_5)_2Si(CH_2)_3NC_5H_{10}$	70	54
5	$(CH_3)_3SiCH_2NH_2$	36	55
6	$(CH_3)_3Si(CH_2)_2NH_2$	46	55
7	$(CH_3)_3Si(CH_2)_3NH_2$	42	55
8	$(CH_3)_3Si(CH_2)_4NH_2$	43	55

The influence of molecular structure factors on the electron-donating capacity of disilazanes[47], cyclosilazanes and cyclogermazanes[48], ethyl(dimethylamino)germanes[50], and dialkylaminochlorogermanes[52] has been investigated. The electron donating capacity diminishes in the sequence C–N–C > Ge–N–Ge ≃ Ge–N–C > Si–N–C > Si–N–Si. The results were interpreted on the basis of a smaller contribution of the effect of the $d_\pi - p_\pi$ interaction in the case of the Ge–N bond compared with the Si–N bond. Infrared spectroscopic data for silylamines[51] and trimethylsilyldiazomethane[53] also indicates the occurrence of d_π–p_π interaction in the Si–N bond.

The electron-donating capacity of organosilicon amines depends significantly on the distance between the silicon and nitrogen atoms[54]. The lower electron-donating capacity of methylsilylamines compared with that of the remaining alkylsilylamines (Table 4, compounds 2–4 and 5–8) is due to the intramolecular interaction of the nitrogen atom and silicon[55]. Similarly the reduced electron-donating capacity of $[(CH_3)_3SiCH_2]_2NH$ [$\Delta\nu$(C–D) = 49 cm^{-1}] compared with $(CH_3)_3SiCH_2N(Alk)H$ [$\Delta\nu$(C–D) ≃ 60 cm^{-1}] is caused, according to the authors[56], by the ($p \rightarrow d$) σ interaction.

2. Electron Donors containing Group VI Elements

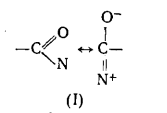
The electron-donating capacity of the oxygen atom in a wide variety of organic compounds has been studied by infrared spectroscopy[9,10,12,15,16,18,54–59,74]. It was established that the electron-donating capacity of the oxygen atom depends significantly on the nature of the substituents linked to it. In the majority of studies[12,60–62] the characteristic features of the variation in electron-donating capacity are considered solely on the basis of qualitative ideas concerning the donor-acceptor properties of substituents (see, for example, Table 7; compounds 1–6).

The formation of hydrogen bonds by a large series of ethers with different electron acceptors has been investigated[12,15]. Correlations were established between the association constant K_{ass} and $\Delta\nu$(O–H) for phenol and also between the shifts of the stretching vibration frequencies ν(X–H) of various electron acceptors for constant electron donors. The electron-donating capacity of dialkoxymethanes R′OCH$_2$OR″ has been characterised in terms of the stretching vibration frequency shift $\Delta\nu$(O–D) for deuteromethanol on formation of hydrogen bonds with the given compounds[63]. $\Delta\nu$(O–D) = 102 cm^{-1} for $(CH_3)_3COCH_2$.$OC(CH_3)_3$. When the t-butyl groups are replaced by the electron-accepting F_3CCH_2 groups, $\Delta\nu$(O–D) decreases to 32 cm^{-1}. The electron-donating capacity of di(β-chlorovinyl)ethers CCl_2 = CH–O–R depends both on the inductive effect of the substituents R and on the p,π conjugation effect. The latter leads to a decrease of $\Delta\nu$ for the given ethers compared with saturated ethers[64].

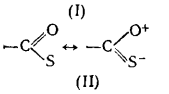
The electron-donating capacity of the carbonyl oxygen atom in the compounds RR_iC = O (for constant R) decreases when R_i changes in the sequence $N(CH_3)_2$ > CH_3 > OCH_3.[65] The relation between $\Delta\nu$(O–H) and the enthalpy of formation of the hydrogen bonds between phenol and diaryl ketones $RC_6H_4COC_6H_4R'$ (where R and R′ = Cl, CH_3, H, or OCH_3) has been investigated; an increase of $\Delta\nu$(OH) for phenol following the enhancement of the electron-donating properties of the substituents R and R′ was noted[67]. The hydrogen bond involving triphenylalkylidenephosphoranes has been investigated[68,69]. As for ketones, the replacement of the methyl group in $(C_6H_5)_3P$ = CH–C(O)CH_3 by the methoxy-group reduces $\Delta\nu$(O–H) for phenol; this is caused by the predominance of the *-I* effect of the methoxy-group over the mesomeric effect[69]. The very strong hydrogen bonds with phenol [$\Delta\nu$(O–H) ≃ 400 cm^{-1}] formed by these compounds have been explained[68] by the delocalisation of the charge:

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H-\underset{\underset{O}{\|}}{C}-R \leftrightarrow (C_6H_5)_3\overset{+}{P}-CH=\underset{\underset{O}{\|}}{C}-R \leftrightarrow (C_6H_5)_3\overset{+}{P}-CH=\underset{\underset{O^-}{|}}{C}-R \quad .$$

The electron-donating capacity of thioesters in the formation of hydrogen bonds with phenylacetylene has also been estimated[66]. Comparison of the results with data for esters and amides showed that the electron-donating capacity of the carbonyl oxygen atom decreases in the sequence amides > esters > thioesters. This can be associated with the fact that structure (I) makes an appreciable contribution to the structure of amides, while structure (II) is significant in thioesters[66]:



(I)



(II)

The electron-donating capacities of cyclic ethers[70], ketones[71], lactones [72], and lactams[73,74] have been studied in a number of investigations. The influence of ring size is reflected in different ways in the electron-donating capacity of the oxygen atom incorporated in the ring or outside the ring. The difference has been explained[70] by the preferential formation of a hydrogen bond with the carbonyl oxygen atom and not with the oxygen atom of the alkoxy-group. However, a spectroscopic study of the hydrogen bonds between esters and trifluoroacetic acid led to the conclusion[75] that both carbonyl and alkoxy-oxygen atoms behave as electron donors.

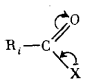
In the above investigations the principal characteristics of the changes in the electron-donating capacity of the oxygen atom in different compounds were interpreted on the basis of qualitative ideas concerning the donor–acceptor properties of the substituents. The details of the changes in the electron-donating capacity, caused by varying the substituents, frequently remained uninvestigated. Studies were therefore undertaken[76,77] to investigate the influence of the inductive and mesomeric effect of the substituents R_i on the electron-donating capacity in relation to compounds of the type R_i–O–R_i and $(R_i)_2C$ = O. The influence of substituents on the electron-donating capacity of the compounds can be characterised quantitatively by the Hammett–Taft σ constants, which are known for the majority of organic substituents†.

For the compounds $(R_i)_2C$ = O, where the substituents R_i exert only an inductive influence on the electron-donating capacity, the following equation was fitted by the method of least squares:

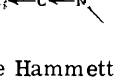
$$\Delta\nu_{ind}(cm^{-1}) = -33\Sigma\sigma^* + 190, \qquad (1)$$

which relates the values of $\Delta\nu$(O–H) for phenol to the sums of the Taft inductive constants σ^* for two substituents R_i.[76] If the substituents R_i are involved in conjugation with the oxygen atom, then the experimental values ($\Delta\nu_{exp}$) differ from those calculated on the assumption of a purely inductive influence of the substituents ($\Delta\nu_{ind}$). The difference $\Delta(\Delta\nu) = \Delta\nu_{exp} - \Delta\nu_{ind}$ characterises the conjugation with the oxygen atom.

Table 5 shows that the experimental values ($\Delta\nu_{exp}$) for the majority of compounds exceed appreciably the values calculated from Eqn. (1) ($\Delta\nu_{ind}$). The reason for the difference $\Delta(\Delta\nu)$ is the p,π conjugation effect:



as a result of which the electron density at the oxygen atom increases. The contribution of this effect rises as X is varied in the series C_6H_5 < OAlk ≃ CH = CHC_6H_5 < $NAlk_2$. On the other hand, the electron-donating capacity of the amides R_i–C(O)–NR_2 decreases as R_i is varied in the series CH_3 > $CH_3CH_2CH_2$ > CH_3CH_2 > C_6H_5 > CH_2Cl > p-$NO_2C_6H_4$.[9] It has been shown[76] that, apart from the p,π conjugation effect, in amides there is yet another mesomeric effect — p,σ conjugation:



† The application of the Hammett–Taft system makes it possible to resolve the influence of electronic effects into components associated with the inductive and mesomeric effects.

Its contribution increases with the $-I$ effect of the substituents R_i.

Table 5. The values of $\Delta(\Delta\nu)$ for the infrared spectra of compounds of the type $(R_i)_2C = O$.

Electron donor	$\Delta(\Delta\nu)$, cm^{-1}	Electron donor	$\Delta(\Delta\nu)$, cm^{-1}
$CH_3COC_6H_5$	+35	$C_2H_5CON(C_2H_5)_2$	+155
$C_6H_5CH=CHCOH$	+76	$CH_3CON(CH_3)_2$	+172
$C_2H_5COOC_2H_5$	+36	$ClCH_2CON(C_2H_5)_2$	+127
$C_6H_5COOC_2H_5$	+51	p-$NO_2C_6H_4CON(C_2H_5)_2$	+143
$CH_2ClCOOC_2H_5$	+38	$Cl_3CCON(CH_3)_2$	+88

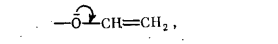
Table 6. The values of $\Delta(\Delta\nu)$ for the infrared spectra of compounds of the type R_i–O–R_i.[76]

Electron donor	$\Delta(\Delta\nu)$, cm^{-1}	Electron donor	$\Delta(\Delta\nu)$, cm^{-1}
$C_6H_5OCH_3$	−38	$CH_2=CHOC_2H_5$	−63
n-$BrC_6H_4OCH_3$	−39	$CH_2=CHOCH_2CH_2Cl$	−55
CH_2-$CHOC_6H_5$	−35	$(C_2H_5)_3SiOCH_3$	−83
$C_6H_5OC_6H_5$	−32	$(CH_3)_3SiOSi(CH_3)_3$	−255
$CH_2=CHOC(CH_3)_3$	−52	$(C_2H_5)_3SiOSi(C_2H_5)_3$	−261

The influences of the inductive and mesomeric effects on the electron-donating capacity of the oxygen atom have been separated by correlation analysis, which was also carried out for the R_i–O–R_i derivatives[76,77]. For compounds with substituents R_i which are not conjugated with the oxygen atom, the values of $\Delta\nu$(O–H) are related to the sum of the Taft inductive constants σ^* for two substituents by the linear equation

$$\Delta\nu_{ind}\,(cm^{-1}) = -90\Sigma\sigma^* + 263. \qquad (2)$$

Table 6 shows that, in compounds with O–C_6H_5 and O–CH=CH_2 fragments, the values of $\Delta\nu_{exp}$ are smaller than those of $\Delta\nu_{ind}$ calculated by Eqn. (2). This is caused by the p,π conjugation effect:



which acts in the same direction as the $-I$ effect of aryl and vinyl substituents. The electron-accepting properties of these substituents therefore become more pronounced and the electron-donating capacity of the oxygen atom in compounds containing the given substituents is weakened. Trialkylsilyl groups have an appreciable $+I$ effect. However, the values of $\Delta\nu_{exp}$ for alkoxysilanes and siloxanes are comparatively small and the differences $\Delta(\Delta\nu)$ are large. The differences are caused by the effect of the d_π–p_π interaction in the Si–O fragments which consist in the delocalisation of the lone electron pairs of the oxygen atom over the vacant $3d$ orbitals of the silicon atom.

Infrared spectroscopic study of the hydrogen bond makes it possible to investigate different aspects of the conjugation effects in organoelemental compounds[78]. Thus studies of the electron-donating capacities of a number of ethers, alkoxysilanes, siloxanes[10,60,62,79–82], alkoxygermanes[61,83,89], and germoxanes[84] showed convincingly that the variation of the electron-donating capacity of the above compounds cannot be accounted for solely by the inductive effects of the substituents and the difference between the electronegativities of the central atoms. A sharp reduction of the electron-donating capacity of the oxygen atom in alkoxysilanes and siloxanes compared with carbon derivatives is a consequence of the shift of the p electrons of the oxygen atom to the vacant $3d$ orbitals of the silicon atom (Table 7; compounds 2 and 7 and 3 and 8). The electron-donating capacity of monoethoxygermanes is greater than that of monoethoxysilanes, which is consistent with the greater d_π–p_π interaction in the Si–O bond compared with Ge–O (Table 7; compounds 7 and 13 and 12 and 17). On the other hand, the values of $\Delta\nu$(N–H) for tetraethoxygermane are only slightly greater than for tetraethoxysilane (Table 7; compounds 11 and 16), which is a consequence, according to the authors[61], of the weaker π bonding to each oxygen atom compared with that in monoethoxysilane. It has been shown[84–86] that the relative electron-donating capacities of silicon, germanium, and tin derivatives vary in the following sequences:

$$SiOC > Si(OC)_2 > Si(OC)_3 > SiOSi;$$
$$GeOGe > GeOC > Ge(OC)_2 > Ge(OC)_3;$$
$$SnOSn > SnOC > Sn(OC)_2.$$

Table 7. The parameters $\Delta\nu$(N–H) for the infrared spectra of hydrogen-bonded complexes (with pyrrole as the electron acceptor).

No.	Electron acceptor	$\Delta\nu$(N–H), cm^{-1}	References
1	$C_2H_5OC_2H_5$	149	62
2	$(CH_3)_3COC_2H_5$	149	62
3	$(CH_3)_3COC(CH_3)_3$	163	62
4	$(CH_3)_2C(OC_2H_5)_2$	138	62
5	$CH_3C(OC_2H_5)_3$	107	62
6	$C(OC_2H_5)_4$	98	62
7	$(CH_3)_3SiOC_2H_5$	138	62
8	$(CH_3)_3SiOC(CH_3)_3$	125	62
9	$(CH_3)_2Si(OC_2H_5)_2$	129	62
10	$CH_3Si(OC_2H_5)_3$	114	62
11	$Si(OC_2H_5)_4$	97	62
12	$(CH_3)_3SiOSi(CH_3)_3$	72	61
13	$(CH_3)_3GeOC_2H_5$	215	61
14	$(CH_3)_2Ge(OC_2H_5)_2$	189	61
15	$CH_3Ge(OC_2H_5)_3$	151	61
16	$Ge(OC_2H_5)_4$	119	61
17	$(CH_3)_3GeOGe(CH_3)_3$	233	84

The electron-donating capacities of cyclic organosilicon compounds with Si–O bonds have also been investigated[87]. The greater values of $\Delta\nu$ for cyclotrisiloxanes compared with cyclotetrasiloxanes can apparently be explained by the more favourable conditions for the d_π–p_π interaction of the lone electron pairs of the oxygen atoms with the d orbitals of silicon in trimers compared with tetramers. The values of $\Delta\nu$(C–D) for alkoxy- and aminoalkoxy-silanes (with deuterochloroform as the electron acceptor) diminish with increase of the number of alkoxy-groups, i.e. with the increase of the $-I$ effect of the latter[88]. The study of the electron-donating capacities of trialkoxysilanes $RSi(OR')_3$ ($R' = CH_3$ or C_2H_5; R is an organic substituent) established a linear correlation between $\Delta\nu$(A–H) for phenol or pyrrole and the Taft inductive constants for the substituents R.[90] This apparently indicates a predominantly inductive mechanism of the influence of the substituents R.

The values of $\Delta\nu$(O–H) for phenol involved in the formation of a hydrogen bond with oxygen-containing organoalkynes $(CH_3)_2(CH_2=CHC\equiv C)COSi(CH_3)_3$ and $(CH_3)_2.(CH_2=CHC\equiv C)SiOSi(CH_3)_3$ indicate a decrease of the electron-donating capacity of the oxygen atom in the sequence C–O–C > C–O–Si > SiOSi.[96,97] The low electron donating capacity of the oxygen atoms in the Si–O and Si–O–Si fragments can be explained by the delocalisation of the electrons of the oxygen atom over the 3*d* orbitals of the silicon atom.

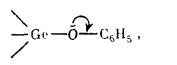
The experimental value of $\Delta\nu$(A–H) for the infrared spectrum of the electron acceptor in many instances characterises an effective electron-donating capacity of the donor in the hydrogen bond and not its true value. The difference between the true and effective values is associated with the steric hindrance of the approach of the electron acceptor molecule to the electron donor centre shielded by bulky substituents. Indeed it has been shown for alkoxy-derivatives of Group IV elements[98,99] that the t-butyl and trimethylsilyl groups give rise to steric shielding of the oxygen atom linked to them, which reduces the experimental $\Delta\nu$(A–H). Allowance for steric factors made it possible to reach a better-founded conclusion concerning the lower extent of the d_π–p_π interaction in the Ge–O bond compared with the Si–O bond.

The application of correlation analysis makes it possible to investigate fairly weak conjugation effects in alkoxy-derivatives of germanium[99]. If the substituents R in $(CH_3)_2Ge(OR)_2$ and $RGe(OC_2H_5)_3$ have only an inductive effect, then the values of $\Delta\nu$(N–H) for pyrrole and the Taft σ^* constants for these substituents are linked by the linear relations (3) and (4) respectively:

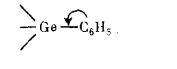
$$\Delta\nu_{N-H}(cm^{-1}) = -47\sigma_R^* + 181, \quad (3)$$

$$\Delta\nu_{N-H}(cm^{-1}) = -44\sigma_R^* + 154. \quad (4)$$

For R = C_6H_5, the corresponding points on the plots deviate from the correlation lines defined by Eqns. (3) and (4). The low values of $\Delta\nu$(N–H) for dimethyldiphenoxygermane are caused by the *p*, π conjugation effect:



and the enhanced electron-donating capacity of triethoxyphenylgermane is due to the effect of the d_π–p_π interaction in the bond, which weakens the electron-accepting properties of the phenyl group[99].



The electron-donating capacities of the organoelemental peroxides $(R_i)_3E–O–O–E'(R_i)_3$ (where E and E′ = C, Si, or Ge and R_i are alkyl or aryl substituents) depend significantly on the inductive effects of the substituents R_i linked to the E and E′ atoms[100]. If E and E′ = Si or Ge, the electron-donating capacity is also determined by the contributions of the effect of the $d_\pi - p_\pi$ interaction, which is more significant for organosilicon compounds and varies non-additively as the number of aryl substituents at the E and E′ atoms is varied.

The influence of the structure on the donor–acceptor properties of certain trialkylsilyl- and germyl-substituted alcohols has been studied[91,92] and it has been established that the electron density at the oxygen atoms in compounds with *n* > 2 in the $(CH_3)_3Si(CH_2)_nOH$ series is independent of the inductive effect of the organosilicon substituent. Evidence for the occurrence of the (*p* → *d*) σ interaction between the oxygen and silicon atoms has not been obtained. According to the values of $\Delta\nu$(O–H) found for phenol, intramolecular coordination takes place in the compounds $(CH_3)_3Si(CH_2)_nOSi(CH_3)_3$ (*n* = 1–4) when *n* = 1; for *n* ≥ 2, the effect is greatly reduced[93]. Among all the compounds investigated, the maximum value of $\Delta\nu$(O–H) was observed for $(CH_3)_3SiCH_2OSi(CH_3)_3$; nevertheless, according to the authors[93], this quantity is unduly low owing to intramolecular coordination, which partially compensates for the +*I* effect of the $(CH_3)_3SiCH_2$ group. The interpretation of the electron-donating capacities of the esters $(C_6H_5)_3ECH_2COOC_2H_5$ does not require the hypothesis of intramolecular coordination between the oxygen atom and the E atom[95]. The low value of the coordination effect and the resulting complications in its study make it at present impossible to regard the above data[91–95] as entirely correct.

The formation of hydrogen bonds by sulphur-containing compounds has been studied by a number of workers. The variation of the frequency and intensity of the ν(S–H) stretching vibration band in the infrared spectra of aliphatic mercaptans demonstrated the presence of a hydrogen bond of the type S–H... S.[101] The formation of hydrogen bonds of the type S–H... Y and X–H... S (X, Y = O, N, or S) in different classes of organic compounds has been examined in a review[102].

The electron-donating capacities of Group VI elements decrease in the sequence O > S > Se > Te. This conclusion was reached in the study of the hydrogen bonds between phenol and the compounds Alk_2X (X = O, S, Se, or Te)[59,103–106]. At the same time there is evidence for a greater electron-donating capacity of the sulphur atom compared with the oxygen atom[105]. In analysing the causes of the discrepancies between the results of these studies, one must take into account the fact that the electron-donating capacity of Group VI atoms depends significantly on the nature of the substituents linked to them[106,107]. Table 8 shows that the shift of the stretching vibration frequency ν(O–H) for phenol on formation of hydrogen bonds by the latter with the derivatives $(n\text{-}C_4H_9)_2X$ diminishes as X varies in the sequence O > S > Se > Te. The values of $\Delta\nu$(O–H) for phenol involved in hydrogen bonding with the $(C_6H_5)_2X$ derivatives diminish for different X in the opposite sequence: Se > S > O.

Table 8. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

X	$(n\text{-}C_4H_9)_2X$		$(C_6H_5)_2X$	
	$\Delta\nu$(O–H), cm^{-1}	References	$\Delta\nu$(O–H), cm^{-1}	Refs.
O	278	103	119	106
S	254	103	151	106
Se	240	103	161	106
Te	220	103	–	–

Apart from the electronegativities of the X atoms, the electron-donating capacity of $(C_6H_5)_2X$ is appreciably influenced by the *p*, π conjugation effect. The effect is a maximum for X = O, which results in a sharp decrease of the electron density at the oxygen atom in diphenyl ether and leads to the inversion of the electron capacity series

for the derivatives $(C_6H_5)_2X$ compared with $(n\text{-}C_4H_9)_2X$. Comparison of the spectroscopic and thermodynamic parameters of the hydrogen bonds between a number of electron acceptors and organic sulphides and selenides showed that the electron-donating capacity depends on the electronegativities of sulphur and selenium atoms and also on the steric and inductive effects of the substitutents[39]. The virtually identical electron-donating capacities of isostructural selenides and sulphides is a consequence of the similar electronegativities of sulphur and selenium atoms[39].

The electron-donating capacity of Group VI elements (X) changes sharply on passing from compounds with the C–X–C fragment to derivatives with the E–X–E group (where E is an element in the silicon sub-group)[42,108,109]. This is associated with the differences between the steric effects of the substituents — mainly with the sharp differences between the inductive effects and with the partial double bond character of the E–X fragments (the effect of the d_π–p_π interaction). The electron-donating capacity of Group VI elements with E = Si diminishes as X varies in the sequence Te > Se > S > O, which is exactly the opposite of the sequence of the electron-donating capacities of X in the Alk_2X derivatives[59,103,104] (see Tables 8 and 9). In series with E = Ge or Sn the maximum electron-donating capacity is shown by oxygen derivatives, but the overall sequence based on the variation of $\Delta\nu$ as a function of the nature of X also differs from the sequence of the given quantities for carbon compounds. These experiments indicate a decrease of the amount of double bond character in the E–X fragments with increase of the atomic number of the elements E and X.

Table 9. The parameters $\Delta\nu$(C–D) (cm^{-1}) for the infrared spectra of the hydrogen-bonded complexes of $[(C_2H_5)_3E]_2X$ (with deuterochloroform as the electron acceptor).[109]

X	E = Si	E = Ge	E = Sn
O	10	47	85
S	29	37	43
Se	31	42	45
Te	42	45	46

In the study of the formation of hydrogen-bonded complexes of the $R_3EXE'R_3$ and R_3EXR' derivatives (E, E' = C, Si, Ge, or Sn; X = O or S) using phenol and indole as electron acceptors the following series based on decreasing electron-donating capacities of the oxygen and sulphur atoms were obtained[110]: SnOSn > GeOGe > SnOSi > COC > SiOSi; SnSSn > GeSGe > SnSSi > CSC > SiSSi; SnOC > GeOC > SiOC; SiSC > SnSC > GeSC. It is noteworthy that the series based on the variation of the electron-donating capacity of the sulphur atom in the compounds R_3ESR' (E = Si, Ge, or Sn), found by Shevchenko et al.[110], differs from the series obtained using deuterochloroform as the electron acceptor[42]. It is known[23,24,98] that the parameter $\Delta\nu$(A–H) can depend on the type of electron acceptor employed, since the steric hindrance in the formation of the hydrogen bond is determined not only by the steric accessibility of the electron-donating centre, which depends on the structure of the electron donor molecule, but also by the dimensions of the electron acceptor molecule.

A correlation between the logarithms of the association constants and the parameter $\Delta\nu$ (A–H) for each electron acceptor was established in the systematic infrared spectroscopic study of the formation of hydrogen-bonded complexes of phosphorus-containing compounds using different electron acceptors[11,111–113]. The electron density in the P = O fragment depends on the inductive and mesomeric effects of the substituents linked to the phosphorus atom. Thus the electron-donating capacity of the oxygen atom in the vinyl-substituted organophosphorus compounds $R_2P(O).CH=CH_2$ decreases in the following sequence for different R: $N(CH_3)_2 \geqslant C_2H_5 > C_6H_5 \geqslant p\text{-}CH_3C_6H_4 > OC_2H_5 > OC_6H_5 > Cl$.[114]

The electron-donating capacities of the arsenic-containing compounds $R_3As=O$ were estimated in the study of their hydrogen bonds with phenol[115,116]. Their electron-donating capacities are much greater than those of the organophosphorus analogues. This is related particularly to the shift of electron density in the P = O fragment towards the phosphorus atom via the d_π–p_π interaction mechanism. In arsenic compounds this effect plays a smaller role.

The study of the electron-donating capacities of the derivatives $R_2S=O$ (R = Alk, AlkO, C_6H_5, or $C_6H_5CH_2$) and nitroso-compounds using phenol as the electron acceptor established a correlation between the parameter $\Delta\nu$(O–H) and the logarithms of the constants for association via hydrogen bonding[117].

It has been shown[118,119] that compounds with the fragments P = S and As = S form hydrogen bonds of the type Ph–O–H...S = X< on association with phenol. The derivatives $R_3As=S$ form stronger hydrogen bonds than the compounds $R_3P=S$, as in the case of the related oxygen-containing compounds[115,116].

Table 10. The parameters $\Delta\nu$(O–H) (cm^{-1}) for the infrared spectra of the hydrogen-bonded complexes of alkyl halides (with phenol as the electron acceptor).

R	F	Cl	Br	I
n-C_4H_9 *	40	59	69	77
n-C_7H_{15} **	40	59	69	71
cyclo-C_6H_{11} *	53	66	82	86

*Solvent–CCl_4.
**Solvent–$CCl_2=CCl_2$.

3. Electron Donors containing Group VII Elements

The formation of intermolecular hydrogen bonds of the type O–H...Hal has been studied by a number of investigators[20,29,103,106,120,121]. Certain data[103,121] are presented in Table 10. With increase of the atomic number of the halogens, their electron donating capacity increases and

the ionisation potentials of the alkyl halides diminish[106]. The stronger hydrogen bonds formed by cyclohexyl halides compared with n-heptyl and n-butyl halides can be explained by the greater $+I$ effect of the cyclohexyl group[121], which entails an increase of the electron-donating capacity of the halogen atom.

The electron-donating capacity of the chlorine atom in $(CH_3)_3ECl$, $(CH_3)_2ECl_2$, and $(CH_3)_3ECH_2Cl$, where E = C, Si, Ge, or Sn, has been measured[122]. For the first two compounds, the electron-donating capacity of the chlorine atom increases in the sequence Si < C < Ge < Sn, which is inconsistent with the variation of the electronegativities of these elements. The anomalously low values of $\Delta\nu$(O–H) for $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ are related to the π-acceptor properties of the silicon atom, i.e. to the effect of the d_π–p_π interaction in the Si–Cl bond. The electron-donating capacity of the Cl atom in the compounds $(CH_3)_3$. ECH_2Cl is almost independent of the nature of the element E and can be accounted for purely by the inductive effect of the $(CH_3)_3ECH_2$ fragments. Thus the possible intramolecular coordination (σ-effect) between the chlorine atoms and E atoms (for E = Si, Ge, or Sn) was not shown under the conditions of the given experiment. Phenol used as the proton donor in the study of the hydrogen bond is fairly nucleophilic and, by solvating the organoelemental compounds at the E atom, it apparently prevents intramolecular coordination between the Cl and E atoms.

4. π-Type Electron Donors

Aromatic compounds having molecular π-orbitals form hydrogen bonds of the type O–H... π on interaction with phenols, alcohols, and other electron acceptors[123,124]. A correlation has been observed[125–127] between $\Delta\nu$(O–H) for the electron acceptor and the ionisation potentials of aromatic π-bases. The principal characteristics of the association of phenol with aromatic compounds have been studied in a number of investigations and the influence of substituents on the stability of the resulting hydrogen bonds has been examined[39,106,120,128–131,142]. The electron-donating properties of the aromatic ring are weakened as the substituents R are varied in the sequence $N(C_2H_5)_2 > OCH_3 >$ Alk $> C_6H_5 > CH_2Cl \sim H \sim C \equiv CH > I \sim Br > Cl > F > CF_3$. The electron-accepting properties of the substituents become more pronounced in the same sequence and can be characterised by the Hammett σ_n constants. The parameter $\Delta\nu$(O–H) of phenol is virtually the same in interaction with naphthalene derivatives as in interaction with the corresponding benzene derivatives[132–134].

The possibility of an increase of the multiplicity of the E–C_6H_5, E–C = C, and E–C $\equiv$ C (E = Si, Ge, or Sn) bonds as a result of the d_π–p_π interaction has been partly considered[43,140]. Comparison of the electron-donating capacities of silicon-containing derivatives of benzene and their carbon analogues (Table 11, compounds 3 and 15 and 4 and 16) shows that the $\Delta\nu$(O–H) of phenol in interaction with arylsilanes are lower, which indicates the operation of the effect of the d_π–p_π interaction in the Si–C_6H_5 fragment.

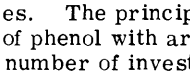
In unsaturated hydrocarbons the most weakly bound electrons are in the molecular π orbitals. Olefins are therefore classified as π-bases. The principal characteristics of the intermolecular association of olefins with phenol and p-fluorophenol have been investigated[131,133,134,135]. The electron-donating capacity of olefins increases with increase of the number of alkyl substituents attached to the sp^2-hybridised carbon atom (Table 12, compounds 1–5).

The nature of the variation of the parameter $\Delta\nu$(O–H) is in general the same as that of the ionisation potentials of the unsaturated hydrocarbons. Indeed, as alkyl substituents at a double bond accumulate, the ionisation potentials of olefins diminish; those of cyclic olefins are much lower than the ionisation potentials of their linear analogues[136,137].

Table 11. The parameters $\Delta\nu$(O–H) for the infrared spectra of the hydrogen-bonded complexes of benzene derivatives C_6H_5X (with phenol as the electron acceptor).[142]

No.	X	$\Delta\nu$(O–H), cm^{-1}	No.	X	$\Delta\nu$(O–H), cm^{-1}
1	$N(C_2H_5)_2$	83	9	H	49
2	OCH_3	62	10	I	39
3	$C(CH_3)_3$	61	11	Br	38
4	$CH(CH_3)_2$	59	12	Cl	35
5	CH_3	58	13	F	30
6	C_6H_5	52	14	CF_3	28
7	CH_2Cl	49	15	$Si(CH_3)_3$	55
8	C≡CH	49	16	$SiH(CH_3)_2$	50

Table 12. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

No.	Electron donor	$\Delta\nu$(O–H), cm^{-1}	References
1	$RCH{=}CH_2$ *	65	135
2	$RCH{=}CHR$ *	90	135
3	$R_2C{=}CH_2$ *	100	135
4	$R_2C{=}CHR$ *	110	135
5	$R_2C{=}CR_2$ *	125	135
6		108	132
7	$(CH_3)_3SiCH{=}CH_2$	56	144
8	$(CH_3)_2SiCH{=}CHCH_3$	84	144
9	$(CH_3)_2SiCH{=}C(CH_3)_2$	116	144
10	$(CH_3)_3SiCH{=}CHC_6H_5$	57	144
11	$(CH_3)_3SiCH{=}CHCl$	29	144
12	$(CH_3)_3GeCH{=}CH_2$	64	144
13	$(CH_3)_3SnCH{=}CH_2$	67	144

* R=Alk.

The above features of the influence of substituents on the electron density at a double bond also obtain for vinyl derivatives of the elements in the silicon sub-group. The increase of the number of methyl groups attached to the sp^2-hybridised carbon atom is accompanied by the additive increase of $\Delta\nu$(O–H) (Table 12, compounds 7–9). The introduction of electron-accepting substituents (the phenyl group, a hydrogen atom, and halogens; Table 12, compounds 7, 10, and 11) leads to a decrease of the π-electron density at the double bond. The electron-donating capacities of derivatives with the E–C = C fragments, where E = Si, Ge, or Sn, increase in the sequence Si < Ge < Sn (Table 12, compounds 7, 12, and 13). This sequence differs from that of the electronegativities of the elements, E, which indicates the operation of mesomeric effects in the organometallic derivatives of ethylene (d_π–p_π interaction). The effect of the d_π–p_π interaction is a maximum in silicon-containing derivatives. This also follows

from a comparison of the values of $\Delta\nu$(O–H) for vinylsilanes and related carbon compounds (see, for example, Table 12, compounds 1 and 7 and 2 and 8).

Phenol also forms hydrogen bonds with cyclopropane derivatives, which behave in many respects like compounds with a double bond[138]. For cyclopropane derivatives, the parameter $\Delta\nu$ is smaller than for alkylbenzenes and monoolefins (~40 cm^{-1}). The low electron-donating capacity of cyclopropane derivatives can probably be accounted for by the comparatively high ionisation potentials (10–9.7 eV) of these compounds[138]. On the other hand, acetylene derivatives exhibit stronger electron-donating properties compared with substituted olefins and alkylbenzenes[131,135,139]. Thus $\Delta\nu$(OH) for phenol hydrogen-bonded to butylacetylene is 90 cm^{-1}, according to West and Kraihanzel[139], and increases to 137 cm^{-1} when the second hydrogen atom is replaced by the ethyl group.

Furan and thiophen derivatives also behave as π-bases in the formation of hydrogen bonds[133,141,143]. Evidently the electron density in the furan and thiophen rings depends significantly on the nature of the substituents. The data presented in Table 13 confirm this convincingly. The introduction of methyl groups greatly increases the electron-donating capacity of furan and thiophen (Table 13; compounds 1–3 and 4–6). The substitution of hydrogen atoms by chlorine leads to a decrease of $\Delta\nu$(O–H) (Table 13; compounds 4 and 7–9). Comparison of the values of $\Delta\nu$(O–H) for organosilicon derivatives and their carbon analogues shows that the electronic effects of the silyl substituents are made up of the inductive effect and effect of the d_π–p_π interaction in the Si–thienyl bond (Table 13; compounds 5 and 10, 6 and 11, and 6 and 12).

Table 13. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

No.	Electron donor	$\Delta\nu_{O-H}$, cm^{-1}	References
1	Furan	48	133
2	2-Methylfuran	66	133
3	2,5-Dimethylfuran	82	133
4	Thiophen	52	133
5	2-Methylthiophen	64	133
6	2,5-Dimethylthiophen	74	133
7	2-Chlorothiophen	39	143
8	2,5-Dichlorothiophen	26	143
9	2,3,5-Trichlorothiophen	15	143
10	2-Silylthiophen	44	143
11	2,5-Disilylthiophen	40	143
12	2-Methyl-5-silylthiophen	57	143

III. INTRAMOLECULAR INTERACTIONS IN ELECTRON ACCEPTORS INVOLVED IN HYDROGEN-BONDED COMPLEXES

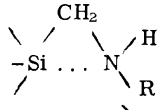
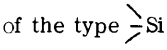
The ability of the hydrogen atom in the AH fragment to form a hydrogen bond of the type AH...X depends both on the type of electron donor X and on the nature of the atom A. If A is a carbon atom, the formation of a hydrogen bond is accompanied by only a slight change in the stretching vibration frequency $\Delta\nu$(C–H)[145–151]. Alkyne derivatives are self-associated via hydrogen bonds with participation of the ≡CH group and the π-electron cloud of the triple bond; self-association leads to a shift of ν(≡CH) by ~10–15 cm^{-1} for alkylacetylenes and ~22 cm^{-1} for phenylacetylene. The change in the stretching vibration frequency of phenylacetylene $\Delta\nu$(≡CH) can be conveniently used as a measure of the electron-donating capacity of carbonyl compounds[66,152]. The electron-accepting capacity of acetylene derivatives has also been studied using *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and ether as bases[139,153]. The introduction of electronegative substituents leads to an enhancement of the electron-accepting capacity of the carbon atom of the ≡CH group. Thus, when the n-butyl group is replaced by the phenyl group, $\Delta\nu$(≡CH) in dimethylacetamide increases from 74 to 91 cm^{-1}.[139] The study of the infrared spectra of alkyne derivatives of the type $R_3EC\equiv CH$ (E is a Group IVB element) in electron-donating solvents showed that silicon and tin compounds form more stable hydrogen-bonded complexes than carbon derivatives[154,155,157]. This is caused by the intramolecular interaction between the π electrons of the triple bond and the vacant *d* orbitals of the elements of the silicon subgroup. Data for the electron-accepting capacity show that the above interaction diminishes with increase of the atomic number of the element of the silicon subgroup. It has been shown for organosilicon derivatives[156] that the electron-accepting properties of the $\equiv CH$ fragment in $R_3Si-C\equiv CH$ depend on the nature of the substituents R. Electron-accepting substituents at the silicon atom increase and electron-donating substituents decrease the mobility of the hydrogen atom and hence the shift $\Delta\nu$(≡CH).

Table 14. The parameters $\Delta\nu$(N–H) for the infrared spectra of hydrogen-bonded complexes (with tetrahydrofuran as the electron donor).

No.	Electron acceptor	$\Delta\nu_{N-H}$, cm^{-1}	References
1	Alk_2NH	~20	5
2	$(C_6H_5)_2NH$	94	15
3	C_4H_4NH (pyrrole)	147	15
4	$AlkNHC(O)CH_3$	~100	5
5	$CH_3NHC(O)OCH_3$	139	163
6	$C_6H_5NHC(O)OCH_3$	153	163
7	$[(CH_3)_3Si]_2NH$	71	162
8	$[(CH_2{=}CH)(CH_3)_2]_2NH$	75	47
9	$C_6H_5(CH_3)_2SiNHSi(CH_3)_3$	76	47
10	$[(CH_3)_2HSi]_2NH$	82	162

We shall now examine data for the electron-accepting capacities of compounds with the NH fragment. Primary amines exhibit a weak electron-accepting capacity. Therefore, in the study of the stretching vibration frequencies of the NH group (ν^s and ν^{as}) in aniline derivatives in electron-donating solvents (acetone, ether, and pyridine), the infrared spectra revealed comparatively small values of the parameter $\Delta\nu$(N–H).[158–161] Thus the ν^{as}(N–H) stretching vibration band in the spectrum of *p*-chloroaniline in acetone undergoes a bathochromic shift by 25 cm^{-1}. If the nitrogen atom forms part of a heterocyclic system, the parameter $\Delta\nu$(N–H) increases (Table 14; compounds 1–3). Therefore pyrrole has been used particularly widely as an electron acceptor in the study of the electron-donating capacities of organic compounds[15,57,61,85].

Table 14 shows that the electron-accepting capacity of the hydrogen atom in the NH fragment depends very significantly on the nature of the two substituents linked to the nitrogen atom. Following the enhancement of the electron-accepting properties of the substituents (Table 14; compounds 1–6), the values of $\Delta\nu$(N–H) increase. The parameter $\Delta\nu$(N–H) is therefore a sensitive indicator of the electronic effects of substituents and can be used in the study of fine details of the changes in these effects, for example, on passing from carbon derivatives to derivatives of silicon subgroup elements[47,48,51,162]. The electron-accepting capacity of silazanes, like that of amines, depends on the nature of the groups at the silicon atom, i.e. on the inductive effect of the silyl groups (Table 14; compounds 7–10). In contrast to alkyl groups, the electronic effects of organosilicon substituents are made up not only of the inductive effect but also of the effect of the d_π–p_π interaction in the Si–N bond. The R_3Si groups therefore become electron acceptors and the mobility of the hydrogen atom in the derivatives $(R_3Si)_2NH$ is appreciably higher than in secondary amines (Table 14; compounds 1, 7, and 10).

The values of $\Delta\nu$(N–H) are also a source of information about other weak intermolecular interactions in organoelemental compounds, for example about the α-effect.[163] The latter obtains in compounds with an $E-CH_2-X$ fragment (E is an element of the silicon subgroup or another atom having vacant orbitals and X is an atom having lone electron pairs) and represents intramolecular coordination, for example,  . In amides and amines containing groups of the type  , the electron-accepting capacity of the hydrogen atom in the NH group depends on the electronic effects of the substituent R linked to the nitrogen atom (the I effect, p,π conjugation, and the α-effect)[163]. The α-effect depends on the nature of the substituents R. When R = Alk, the α-effect is a maximum; it decreases for R = C_6H_5 owing to competition with the effect of p,π conjugation; when R = $C(O)OCH_3$, there is no α-effect.

A large number of spectroscopic studies of the formation of hydrogen bonds with participation of OH groups and various electron donors have been made[12,15,67,96,106,164–178]. The electron-accepting capacity increases after the introduction of electron-accepting substituents into the molecule. Thus the O–H stretching vibration frequency shift $\Delta\nu$(O–H) in the infrared spectrum of tetrafluoropropanol dissolved in acetone is 165 cm^{-1}, while the corresponding shift for propanol is only 110 cm^{-1}.[67] The electron-accepting capacity of chloroalcohols increases as chlorine atoms accumulate in the molecule[168,169]. However, the electron-donating capacity of alcohols then diminishes, which induces a decrease of the degree of self-association of chloroalcohols. Thus the ν(O–H) stretching vibration band of $(CCl_3)_2CHOH$, corresponding to an associated species formed via an intermolecular hydrogen bond, is not observed even at an alcohol concentration of ~2 M.

The electron-accepting properties of phenol derivatives can be regulated over a wide range by varying the nature of the substituents in the aromatic ring[171–173]. The introduction of electron-accepting substituents in the p-position in phenol increases the mobility of the hydrogen atom of the OH group. $\Delta\nu$(O–H) for phenol in diethyl sulphide is 256 cm^{-1}, increasing to 280 cm^{-1} for p-chlorophenol[105].

The stretching vibration frequency of the S–H bond changes little on formation of a hydrogen bond. It was therefore believed for a long time that the self-association of the corresponding compounds via the formation of hydrogen bonds of the type S–H. . . S does not occur. However, subsequently the presence of hydrogen bonds of this type was demonstrated and certain characteristics of the formation of such hydrogen-bond complexes were investigated: the dependence of the electron-accepting capacity of the S–H group in p-substituted thiophenols on the nature of substituents[179]; the presence of a hydrogen bond of the type S–H. . . S in aliphatic thiols and of the type S–H. . . S and S–H. . . π in benzenethiols and α-toluenethiols[180]; the formation of a hydrogen bond between mercaptans RSH and amines, ethers, and thioethers[101]. Comparison of the electron-accepting capacities of the OH and SH groups in the formation of an intermolecular hydrogen bond showed that the hydrogen in thioacids is less mobile[181,182]. The greater shielding at the proton in the SH group is normally due to the more diffuse nature of the orbitals of the outer electrons of the sulphur atom compared with the outer orbitals of the oxygen atom[182].

Table 15. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with tetrahydrofuran as the electron donor).

No.	Electron acceptor	$\Delta\nu$(O–H), cm^{-1}	References
1	$(C_6H_5)_3COH$	208	140
2	$(C_6H_5)_3SiOH$	338	140
3	$(C_6H_5)_3GeOH$	211	140
4	$(C_6H_5)_3CCH_2OH$	140	187
5	$(C_6H_5)_3SiCH_2OH$	160	187
6	$(C_6H_5)_3GeCH_2OH$	170	187
7	$(C_6H_5)_3CCH_2CH_2OH$	165	187
8	$(C_6H_5)_3SiCH_2CH_2OH$	155	187
9	$(C_6H_5)_3GeCH_2CH_2OH$	160	187
10	$(C_6H_5)_3COOH$	330	190
11	$(C_6H_5)_3SiOOH$	408	190
12	$(C_6H_5)_3GeOOH$	335	190
13	$(C_6H_5)_3SnOOH$	258	190

The formation of hydrogen-bonded complexes by organoelemental compounds of Group IVB elements was first studied[140,183–185] in relation to alcohols of the type R_3EOH and $(C_6H_5)_3EOH$, where E is an element of the silicon subgroup. Diethyl ether, mesitylene, and tetrahydrofuran were studied as electron donors. Compared with the corresponding carbinols, silanols exhibit much greater shifts $\Delta\nu$(O–H) (Table 15, compounds 1–3). The series corresponding to the diminution of the electron accepting properties of alcohols as a function of the element E(Si > Ge ≃ C > Pb ≃ Sn) does not agree with the electronegativity series of these elements. Taking into account only the inductive effect, it was to be expected that the greatest electron-accepting capacity would be shown by carbinols and germanols. On the basis of these data, it was concluded[140,183–185] that the d_π–p_π interaction takes place in the E–O fragments, its intensity diminishing as E is varied in the sequence Si > Ge > Sn > Pb. The greater electron-accepting capacity of vinylacetylenic silanols compared with their carbon analogues can also be explained by the d_π–p_π interaction between the oxygen and silicon atoms[96]. The greater electron-accepting capacity

of silanethiols compared with the corresponding thiols is due to the delocalisation of the lone electron pair of the sulphur atom over the 3*d* orbitals of the silicon atom, which increases the mobility of the hydrogen atom in the Si–S–H fragment[186].

The electron-accepting capacity of the hydrogen atom in the test compounds decreases in the sequence $(C_6H_5)_3$. .SiSH ≫ C_6H_5SH > $(CH_3)_3SiSH$ > $(C_6H_5)_3CSH$ > $(CH_3)_3CSH$, which is analogous to the sequence based on the decrease of the mobility of the hydrogen atom of the given group in oxygen-containing compounds: $(C_6H_5)_3SiOH$ ≫ C_6H_5OH > $(CH_3)_3SiOH$ > $(C_6H_5)_3COH$.[184] In the series of alcohols $(C_6H_5)_3ECH_2OH$ the electronegativities of the Group IVB elements E suggested that the carbinol should have the greatest electron-accepting capacity. However, the experimental electron-accepting capacity series for the alcohols is different: $(C_6H_5)_3GeCH_2OH$ > $(C_6H_5)_3SiCH_2OH$ > $(C_6H_5)_3CCH_2OH$ (Table 15, compounds 4–6). This fact can probably be accounted for by an intramolecular coordination of the type $(p \rightarrow d)\sigma$ between the oxygen and germanium atoms as a result of the existence of the vacant 4*d* orbitals in the latter. In the silicon derivative this effect is less pronounced and in the carbon derivative it is altogether absent. The nature of the element E has almost no influence on the mobility of the hydrogen atom in the alcohols $(C_6H_5)_3ECH_2CH_2OH$,[187] because the inductive effect of groups $(C_6H_5)_3ECH_2CH_2$ changes only slightly as E is varied (Table 15, compounds 7–9). There is apparently no intramolecular coordination in these compounds.

In the study of the electron-accepting properties of the silicon containing alcohols $(CH_3)_3Si(CH_2)_nOH$ and $R(CH_3)_2$. .$SiCH_2OH$ (n = 1–4, R = C_2H_5 or C_6H_5) the authors[91,188] concluded that there is no intramolecular interaction in these compounds between the oxygen and silicon atoms. However, intramolecular interaction does take place in the compounds $C_6H_5(CH_3)_2Si(CH_2)nOH$ (n = 1, 2) and $(C_6H_5)_3$. .$SiCH_2OH$.[188] This interaction apparently involves the formation of an intramolecular hydrogen bond, since in the carbon analogues the effect is more marked.

When the electron-accepting capacities of organosilicon hydroperoxides, carbinols and silanols and organic hydroperoxides were compared, the following series were obtained[189]: R_3COH < R_3SiOH, R_3COH < R_3COOH, $(CH_3)_3$. .EOH < $(C_6H_5)_3EOH$ (E = C or Si); R_3SiOH < R_3SiOOH, $(CH_3)_3SiOOH$ < $(C_6H_5)_3SiOOH$, R_3COOH < R_3SiOOH (R = CH_3 or C_6H_5). The results indicate the operation of the effect of the d_π–p_π interaction in the Si–O bond.

The electron-accepting capacity of the hydroperoxides $(C_6H_5)_3EOOH$ (E = C, Si, Ge, or Sn) decreases in the sequence $(C_6H_5)_3SiOOH$ > $(C_6H_5)_3GeOOH$ > $(C_6H_5)_3COOH$ > $(C_6H_5)_3SnOOH$ (Table 15, compounds 10–13). This leads to an electronegativity series of Group IV elements, Si > Ge > C > Sn, which differs from the corresponding series in the absence of conjugation effects: C > Ge > Si ≈ Sn.[191] This discrepancy between the electronegativity series can be accounted for by the effect of the d_π–p_π interaction, which diminishes in the sequence Si > Ge > Sn.

* * *

Thus the parameter $\Delta\nu$, which can be most readily determined experimentally from the infrared spectrum, serves at the same time as a source of fairly extensive information both in a qualitative assessment of the weak effects of substituents in the molecules involved in the hydrogen bond and in a semiempirical study of the effects using the Taft–Hammett system. This method for the investigation of intramolecular interactions has been by no means exhausted in the study of organic compounds; a quantitative theory relating the parameter $\Delta\nu$ to molecular structure factors will probably be created in the future. The simplicity and clarity of the method makes it promising for the study of organoelemental compounds, where the inadequate development of the theory of chemical bonding frequently restricts the employment of complex research techniques.

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The Formation of Coatings in the Anodic Electrodeposition of Water-Miscible Lacquer Systems

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The physicochemical principles of the formation of polymeric coatings in the electrodeposition of water-miscible compositions based on carboxyl-containing oligomeric electrolytes are described. The mechanism of the formation of the deposit on the anode and the film formation processes on various metallic supports are considered.
The influence of the composition of the system and the deposition conditions on the electrodeposition mechanism and the properties of the coatings are discussed. It is shown that electrodeposition is one of the ways of creating an ordered structure in the formation of polymeric coatings, which ensures a higher rate of relaxation processes.
The bibliography includes 104 references.

CONTENTS

I. Introduction 1212
II. Characteristic features of the formation of coatings in the electrodeposition of water-soluble film-forming agents 1212
III. The mechanism of the electrodeposition of the pigment component of water-miscible lacquer materials. 1218
IV. The influence of electrodeposition conditions on the formation of a deposit on the anode and the properties of the coatings 1220

I. INTRODUCTION

Lacquer coatings are thin polymeric films bound to the support by adhesion forces. The mechanism of their formation includes the formation of local bonds between the active groups of the polymer molecules and the surface of the support. This results in a retardation of the relaxation processes and the occurrence of internal stresses which lower the lifetime of the coatings. The rate of relaxation processes and the cause of the stresses depend on the conformations of the molecules in solution, on the nature of the supermolecular structures arising in the coating at a particular stage in the formation of macromolecules, and also on the number and nature of the bonds between them.

This review deals with the formation of coatings from water-miscible lacquer materials based on water-soluble oligomeric electrolytes when they are electrodeposited on a support[1,2]. This is a new method of colouring, which appeared at the beginning of the 1960's as a special procedure for the deposition on a metal of aqueous lacquer systems[3-9], whose application has been extremely limited hitherto owing to the difficulty of their conversion into a coating in view of the specific features of water as a solvent. A characteristic of this method of colouring, in contrast to traditional methods based on the evaporation of solvents, is that the coatings are formed in two stages. Initially a water-insoluble deposit is formed on the anode in the field of a direct current, the anode consisting of the article to be coloured, and subsequently, in the course of thermal hardening, a three-dimensional network is formed from the virtually dehydrated oligomeric system. The review deals with the mechanisms of the processes occurring in this system.

II. CHARACTERISTIC FEATURES OF THE FORMATION OF COATINGS IN THE ELECTRODE POSITION OF WATER-SOLUBLE FILM-FORMING AGENTS

1. The Formation of a Deposit on the Anode

The film-forming agents used as binders in lacquers for electrodeposition consist of water-soluble carboxyl-containing oligomeric electrolytes. Their acid form is weakly dissociated; after the neutralisation of the carboxy-groups by organic amines (ammonia), they become water-soluble and capable of dissociation via the mechanism[7]

$$RCOONH_4 \rightleftarrows COO^- + NH_4^+ \quad ,$$

where $RCOO^-$ is the film-forming component converted into the anionic form. The diphilic structure of the molecules of the film-forming agents makes it possible to compare them with a set of low-molecular-weight surfactants whose hydrophobic component consist of a polymer (oligomer) chain and the hydrophilic component consists of COOH groups.

It has been established, on the basis of the surface tensions, electrical conductivities, and light scattering in aqueous solutions of a number of film-forming agents as a function of concentration[10], that aqueous solutions of neutralised film-forming agents at the concentrations used for electrodeposition (6–10%) are either micellar solutions containing ionised micelles (together with individual ions) or polyelectrolytes, in which neutral molecules (or their associated species) and ions are involved in an equilibrium controlled by the dissociation constant. In the first stage

of the development of the method of colouring by electrodeposition the mechanism of the formation of the deposits on the anode from such systems was obscure.

Numerous studies were carried out during this period and general hypotheses were put forward concerning the process mechanism, by analogy with galvanic processes as well as the electrophoretic process for the formation of coatings[11-19]. It was to be expected that the segregation on the anode of a polymer phase from the solution of a carboxyl-containing polyelectrolyte is associated with electrochemical processes in the region near the electrode under the influence of the electric current.

Anodic processes in an aqueous medium have been thoroughly investigated in relation to a number of metals[20-22]; in the case of metals incapable of being passivated these involve anodic dissolution:

$$M \rightarrow M^{n+} + ne \quad , \qquad (1)$$

while in the case of metals which can be passivated as well as certain inert electrodes such as platinum and graphite the relevant process involves the electrolytic dissociation of water:

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e \qquad (2)$$

At high pH values reaction (2), which can occur in solutions at pH $\leq$ 11.5, is replaced by the discharge of hydroxide ions:

$$2OH^- \rightarrow 1/2O_2 + H_2O + 2e \quad . \qquad (3)$$

Apart from reactions (1)–(3), other electrochemical processes can occur on the anode in the electrodeposition of water-soluble film-forming agents—anodic oxidation of the metal (for example in the colouring of aluminium) as well as the decarboxylation and oxidation reactions of the organic molecules:

$$2RCOO^- \rightarrow R{-}R - + 2CO_2 + 2e \quad , \qquad (4)$$

$$RCOO^- + H_2O \rightarrow ROH^- + CO_2 + 2e \quad , \qquad (5)$$

$$\overset{|}{-}CH_2 + \cdot H_2O \rightarrow HCOH + 2H^+ + 2e \quad . \qquad (6)$$

It is believed[23] that the formation of a deposit on the anode under the electrodeposition conditions takes place as a result of the electrochemical discharge of the anions of the film-forming agent associated with decarboxylation as in the Kolbe synthesis in accordance with reaction (4).

Beck[24,25] calculated the change in the concentration of hydrogen ions in the anodic compartment during the electrodeposition of water-soluble oligomers. In the electrodeposition from solution at pH 8 and a current density of 2.5 mA cm^{-2} the pH in the anodic compartment falls to 2, which corresponds to (or is lower than) the pH at which deposits are formed in the electrodeposition of anionic water-soluble film-forming agents.

In order to elucidate the mechanism of the formation of the deposit on the anode in the electrodeposition of water-soluble film-forming agents (in relation to VBFS-4 resin, VML oil, rezidrol and water-soluble acrylic carboxyl-containing film-forming agents), the chemical composition of the films electrodeposited on anodes made of different metals was analysed by infrared spectroscopy (before thermal hardening).[29-30,44] It was established that, in the electrodeposition of the film-forming agents on anodes made of metals such as copper, cadmium, and zinc, the products are predominantly the salts of the binders, while in the electrodeposition on insoluble anodes and on steel mainly their acid form is produced. The acid form of the film-forming agents is produced as a result of their interaction with the H^+ ions generated in the anodic compartment by reaction (2), while the formation of the salt form is associated with reaction (1). It was observed that a steel anode dissolves at the rate of 0.25 and 0.18 g m^{-2} min^{-1} in the electrodeposition of the FL-149E enamel and the FL-093 primers respectively. Chemical analysis established the presence of iron in the electrodeposited film. X-Ray diffraction analysis showed that the thermally hardened coating contains iron in the form of the oxides Fe_2O_3 and Fe_3O_4 and not as products of the interaction with the film-forming agents. The oxides were probably formed during drying from the iron hydroxides deposited on the anode.

It has been suggested[27] that the difference between the mechanisms of electrodeposition on anodes of different types can be accounted for by the different solubilities of the salt and acid forms of the film-forming agents, on the one hand, and the hydroxides of the metal of the support, on the other. According to the solubility products (SP) of the hydroxides, iron(III) hydroxide is deposited most readily ($SP_{Fe(OH)_3} = 3.8 \times 10^{-38}$), while zinc hydroxide is deposited with the greatest difficulty ($SP_{Zn(OH)_2} = 5 \times 10^{-7}$). The concentration of the metal ions at the copper, cadmium, zinc, and other metal anodes is sufficient for the deposition of the binders in the salt form. It is noteworthy that the electrodeposition of the VML oil and rezidrol is accompanied by the partial oxidation of the double bonds, as shown by the decrease (up to complete disappearance) of the bands at 3020 and 997 cm^{-1} in the spectra of the resulting electrodeposited films.

In the electrodeposition of acrylic film-forming agents[28-30] the deposit is produced on the steel anode as a result of the interaction of the film-forming agent with both hydrogen and metal ions produced in the anodic dissolution of the electrode. If the electrodeposition is carried out on a steel anode over a long period (>3 min), then in the case of rezidrol the deposit is found to contain a certain amount of the salt form owing to the secondary interaction between the acid form of the film forming-agent produced and the metal hydroxides present in the film.

Thus the mechanism of the formation of a deposit on the anode (as the acid or salt form of the film-forming agent) depends on the nature of the metal on the surface being coloured, the chemical composition of the film-forming agent, and the conditions of the electrodeposition process (i.e. is determined by the solubility of the acid or salt form of the film-forming agent under the given electrodeposition conditions). The mechanism of the electrodeposition consists in the loss of solubility by the film-forming agent in the anodic compartment on interaction with the hydrogen or metal ions formed as a result of the primary electrochemical reactions in the electrolysis of water and the anodic dissolution of the metal. Reactions (4) can take place only on insoluble anodes at a rigorously defined temperature and pressure[31]. Oxidation of the film-forming agent plays an insignificant role. Furthermore, the discharge of ions on the surface of the anode should have ceased immediately after the segregation of a monomolecular organic layer, lacking in electronic conductivity, which was not confirmed by observations on the growth of the thickness of the coating.

Analysis of the composition of the gas involved on the anode[32-34] and the determination of the range of electrode potentials[35-38] at which electrodeposition takes place established that the current is mainly consumed in reactions (1)–(3). The partial oxidation at the anode of the

amines used as neutralisers of the film forming agents can also be included among secondary reactions[32,38]. This mechanism of the formation of a deposit on the anode agrees satisfactorily with the fundamental electrochemical studies of the electrodeposition of carboxyl-containing polyelectrolytes carried out in recent years[35-38]. These data established that, in the electrodeposition of polyelectrolytes on steel and also on phosphated steel, the main electrode reaction in the absence of activators of anodic dissolution is evolution of oxygen as a result of the oxidation of water molecules; at the same time the binder may be oxidised, which also leads to the formation of H^+ ions in the region near the anode.

Since the solution is stirred in the course of the electrochemical decomposition, the bath with the working solution may be regarded as a volume with a constant concentration[36]. A difference between concentrations is observed only at the interface where a diffuse double layer (Nernst layer) is "stuck" to the electrode. In this quasi-stationary layer species are transported via diffusion, which arises owing to the concentration gradient due to the discharge of the ions on the electrode and the migration of protons to the cathode as well as the migration of ions under the influence of electrical forces. Calculations have shown[36] that the thickness of the anodic layer of hydrogen ions is 10^{-2} cm. The film-forming agent loses its solubility in water on interaction with the precipitant ions in the layer near the anode. The deposits formed on the anode are highly concentrated two-phase systems. These are colloidal structures consisting of globular particles, whose size varies from 0.1 μm to several hundred μm, depending on the type of the film-forming agent and the process conditions[39,40].

The electrodeposition process takes place in a relatively dilute medium (6–15%), but the electrodeposits consist of highly concentrated systems. The dry residue of the electrodeposited films amounts to 94–98% and the electrodeposition conditions have only an insignificant influence on this proportion[36,39,40]. The hypothesis of the decisive role of electroosmosis in the mechanism of the dehydration of anodic deposits, which remained current for a long time, was not confirmed when the degree of electroosmotic dehydration was calculated from electrochemical equations[36] although electroosmosis undoubtedly takes place. Since the system passes through a metastable state on formation of a deposit, water is evidently removed also as a result of syneresis. The deposit is dehydrated also in consequence of the decomposition of water in the diffuse layer near the anode[36]; the protons evolved are transported through the film via diffusion and migration. According to Beck's view[36], the negative ions of the film-forming agent still fixed in the deposit can be regarded as bound to mobile protons, as happens in weakly acidic ion-exchange resins; the protons are expelled to the surface of the film, which ensures an increase of its thickness.

When the process is carried out under the conditions of a constant current density (galvanostatic conditions), the rate of electrodeposition can be expressed by adding the weight of the deposit on the anode per unit time. The overall form of the experimental time variation of the increment in the weight of the deposit is illustrated in Fig. 1*a* for a number of film-forming agents[36,38,39]. The relation along section *1* (Fig. 1*a*) is linear, but the corresponding straight line does not pass through the origin of coordinates. The induction period at the beginning of the process, where the coating is not formed, is necessary to create in the anodic compartment a concentration of H^+ of M^+ ions sufficient to precipitate the film-forming agent. The induction period and the slope $\tan\alpha$ depend on the nature of the film-forming agent and on the process conditions. For the same film-forming agent in a bath without stirring, there is a qualitative relation between the duration of the induction period and the reciprocal of the square of the current density. Theoretically one gram-equivalent of the precipitant ions evolved in the electrochemical reaction should neutralise one gram-equivalent of the macroanions. Thus

$$q = 5.6 \times 10^6/\text{A.N.} \times aF, \qquad (7)$$

where A.N. is the acid number of the film-forming agent (mg KOH/g resin), a the degree of neutralisation, and F the Faraday. Hence it follows that the quantity q, called the "conventional current yield", should be a constant characterising the given carboxyl-containing polyelectrolyte. However, experimental tests showed[36-39] that q and $\tan\alpha$ (for the given current density) depend on the concentration of the film-forming agent, the stirring conditions in the bath, the pH, temperature, the conversion of the film-forming agent into an insoluble state on partial neutralisation of the ionised carboxy-groups, the polydispersity with respect to the molecular weight and composition, etc. It has been established for acrylic film-forming agents[41,42] that, with increase in the number of carboxy-groups in the copolymer per unit molecular weight, in the degree of neutralisation of the binder, in the pH of the system, in the rate of stirring, and, when the temperature is reduced, also with increased current density[40], the induction period increases and $\tan\alpha$ falls.

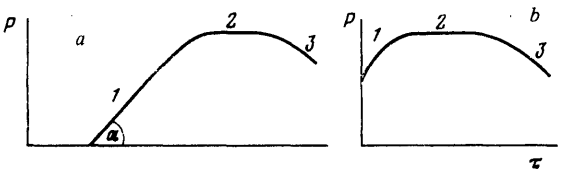


Figure 1. Schematic illustration of the dependence of the increment in the weight of the deposit on the anode P as a function of the process time τ [7,29,41] under different conditions: *a*) i = const.; *b*) u = const.

When the process is carried out under constant-potential conditions (potentiostatic conditions; Fig. 1*b*), there is a high initial current density, so that the induction period does not play an important role along section *1*. The thickness of the coating increases with time. Along section *2*, the thickness of the film does not increase for a long time (up to 5–10 min, depending on the type of film-forming agent and current density) and then begins to decrease (section *3*). The retardation of film growth is attributed[36] to the hindrance of ion transport through the film, which is regarded as the rate-limiting process. The presence of maxima and minima on the $i(\tau)$ and $u(\tau)$ curves has been observed by a number of workers[35,36,43] and some of them believe that this is caused by dielectric breakdown[44]; other studies established a relation between the heat evolution in the film and the existence of the extrema[43,45]. It has been observed[40,46] that the presence of section *3* on the curves in Figs. 1*a* and 1*b* is associated

with the stripping of the deposit from the anode owing to the increase of the amount of heat evolved during the electrodeposition. This was established in a study of the structural-mechanical properties of the films formed on the anode under different electrodeposition conditions.

2. The Influence of Structural-Mechanical Properties of the Film-Forming Agents on Their Electrodeposition

The formation of polymeric coatings proceeds via a structure formation stage[1-5]. The structure formation in the solution from which the coating is produced influences the rate of inhibition of relaxation processes. During electrodeposition, a structure is produced on formation of the deposit on the anode before the onset of thermal hardening. The ability of the system to give rise to relaxation processes, on which the formation of monolithic defect-free films depends, can be inferred from structural-mechanical properties.

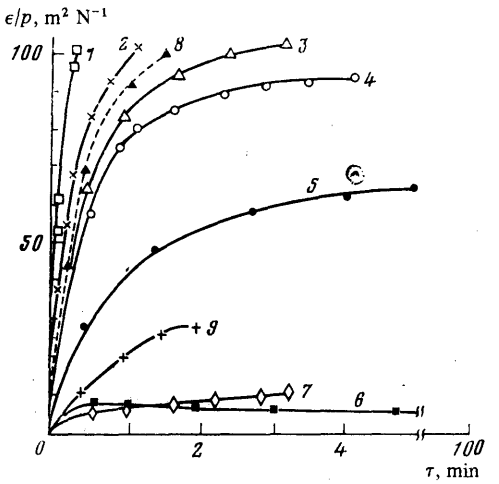


Figure 2. The development of the shear deformation (ϵ/p) of the electrodeposits with time (t) ($p = 2$ N m^{-2}):[46] 1) VML oil; 2) VA-105 rezidrol; 3) VA-133 rezidrol; 4) polyacrylate + 3% butanol; 5) polyacrylate + 2% butanol; 6) polyacrylate without butanol ($p = 20 \times 10^3$ N m^{-2}); 7) VBFS-4 resin + 3% of 2:1 mixture of butyl and isopropyl alcohols; 8) VBFS-4 resin + VML oil + 3% of 2:1 mixture of butyl and isopropyl alcohols; 9) VBFS-4 resin + VML oil with a reduced content of solvents.

In the formation of coatings by the electrodeposition method the structural-mechanical properties of the deposits on the anode play a special role associated with their influence on the mechanism of the electrical insulation of the anode. The rheological characteristics of the electrodeposits obtained from systems of water-soluble film-forming agents, differing in their chemical nature and in the presence of added organic solvents, have been investigated[45-47]. The form of the deformation curves (Fig. 2) leads to the conclusion that the electrodeposits exhibit different rheological properties. Thus deformation curves for rezidrol and acrylic film forming-agents containing added organic solvents have sections with conventional instantaneous elastic and plastic deformation, while the VML oil flows and the VBFS-4 resin is not deformed at all owing to its brittleness. The capacity for deformation of acrylic film-forming agents without added organic solvents is weak. There is a corresponding difference in the behaviour of the above systems in electrodeposition. Monolithic defect-free films are formed from rezidrol and the VML oil. The electrodeposition of the VBFS-4 resin and acrylic film-forming agents from systems without organic solvents leads to the formation of thin porous coatings. When organic solvents are added to these systems, the nature of the porosity changes. With increase in the amount of solvent in the system, the pores ("craters") in the coating become smaller and then disappear altogether. Under these conditions, the electrical resistance of the anode diminishes and there is a corresponding increase in the thickness of the coating. The introduction of organic additives into the system based on the VML oil (the deposit exhibits an appreciable irreversible deformation) leads to the formation of bulges on the coating and to a decrease of the electrical potential during deposition.

The increased hindrance to the coalescence of the electrodeposited species with increasing rigidity of the film-forming agent leads to the retardation of the removal of oxygen bubbles from the surface of the anode, to an increase in the resistivity of the latter, and to the consequent formation of thin porous coatings (the pores are sites where oxygen bubbles are located)[47-51]. Conversely factors promoting the coalescence of particles (for example, the introduction of organic solvents plasticising the electrodeposits) causes an increase of the capacity of the system for undergoing relaxation processes, which leads to the "healing" of the pores, to a decrease of the resistivity of the anode, and to an increase of the thickness of the coatings. However, a high plasticity of the system is also undesirable from the standpoint of the electrodeposition process. This has been shown[46] by comparing the VML oil, the VA-105 rezidrol, and the VA-133 rezidrol, which differ in the rheological characteristics of their electrodeposits and the deposition parameters (Fig. 3).

Direct measurement of the temperature of the anode during the electrodeposition process with the aid of a Chromel–Copel thermocouple welded into the anode established[43] that during electrodeposition the temperature of the anode rises up to 70–80°C depending on the electrical parameters. Such heating in the case of the highly plastic VML oil (Fig. 3) leads to the formation of bulges on the surface of the coating and, on further increase of the potential, the coating flows off the surface of the anode. The optimum potential in the electrodeposition of the VML oil is 30–40 V. The high viscosity of the rezidrol deposit (Figs. 3*b* and 3*c*) makes it possible to increase the potential considerably during electrodeposition (up to 300 V) for the VA-133 rezidrol.

Thus a significant factor in the formation of coatings by electrodeposition is the viscosity of the deposit formed for low shear stresses. From this it also follows that one of the causes of the differences between films electrodeposited from high-resistance lacquer materials at high potentials (hundreds of volts) and low-resistance materials (deposition potential of tens of volts) consists in the difference between the structural-mechanical properties of their deposits, which play an important role in the mechanism

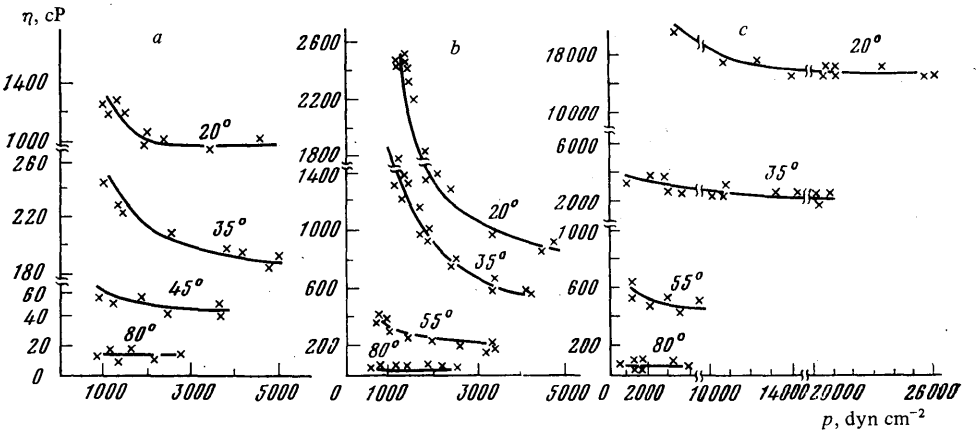


Figure 3. Dependence of the viscosity η of electrodeposits based on different materials as a function of the stress p corresponding to the slipping of the deposits[46]: *a*) VML oil; *b*) VA-105 rezidrol; *c*) VA-133 rezidrol.

of the electrical insulation of the anode during electrodeposition[45].

3. The Mechanism of Film Formation in the Electrodeposition of Water-Soluble Film-Forming Agents

(a) The influence of the method of deposition of water-soluble film-forming agents on the support. It has been established by infrared spectroscopy that the mechanism of film formation in the production of coatings by methods based on the evaporation of solvents (pouring, spraying) and on electrodeposition is in principle the same at the molecular level and is associated mainly with oxidative polymerisation (VML oil[27], rezidrol[52]), with formation of ester linkages via carboxy- and hydroxy-groups (VML oil, VBFS-4 resin, and partly rezidrol), and also (in the case of acrylic film-forming agents) the interaction of hydroxymethyl groups with carboxy- and amide groups[53]. However, in electrodeposition the formation of a three-dimensional network takes place to a greater extent than in the formation of coatings by pouring and the difference is greater the lower the hardening temperature (Table 1).

Electron microscope study of coatings has shown that electrodeposited coatings are structurally more homogeneous and that the size of the structural elements and the distance between them is smaller than in the formation of coatings by pouring or spraying (Fig. 4). With increase of the hardening temperature, the size of the structural elements of the coating and the distance between them diminish, but in electrodeposition there is a greater number of structural elements per unit surface than in the pouring method over the entire experimental temperature range (from 20° to 250°C). Owing to the smaller dimensions of the structural aggregates, better conditions are probably established in electrodeposition for a more complete interaction between the structural elements on the surface via the reactive groups than in the pouring method. Apart from the smaller size of the structural elements of the coating, the acceleration of the film formation process in electrodeposition is associated with the regeneration of the reactive carboxy-groups on formation of a deposit on the anode (in the pouring method this occurs only during thermal hardening) and also, in the case of oily binders, with the preliminary oxidation of the film-forming agent on the anode.

Table 1.* Dependence of the molecular weight of the section of the chain between the effective nodes of the three-dimensional network (M_C) in the formation of rezidrol coatings on the hardening temperature[52].

Method of colouring	Hardening temperature			
	130°	180°	200°	220°
Pouring method	3792	975	371	308
Electrodeposition method	371	280	241	238

The presence of a homogeneous fine globular structure of the electrodeposited coating creates conditions better than in other deposition methods for the acceleration of relaxation processes. This is confirmed by data obtained in the study of the thermal conductivities of coatings. It has been established[27] that the thermal conductivities of electrodeposited coatings are greater than those of the coatings formed by spraying or pouring. As a result, the electrodeposited coatings have smaller internal stresses and hence better physicomechanical properties. Indeed, the resistance to wear and adhesion are superior in electrodeposited coatings to those of coatings obtained by the pouring and spraying methods[52]. The available literature data[54], suggesting that the properties of coatings obtained by electrodeposition and spraying do not differ, are based on a comparison of properties of coatings which, although obtained from water-soluble systems, were produced in different media (a comparison was made of coatings obtained by electrodeposition from an aqueous medium and deposited by spraying from an acid paste diluted with organic solvents). Tests on the protective properties of the coating showed that electrodeposited

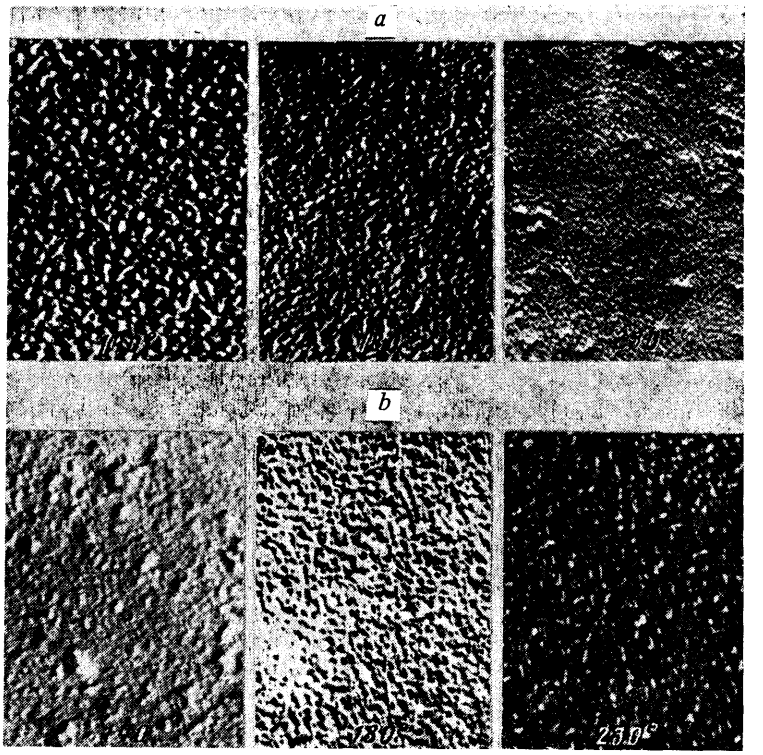


Figure 4. Electromicroscope structure of coatings based on rezidrol[52]: *a*) formation by electrodeposition; *b*) formation by the pouring method. Magnification 1 × 32 000

coatings exhibit a more satisfactory resistance to water and salts than films produced by other deposition methods[52].

All these factors suggested a longer lifetime of the electrodeposited coatings compared with those produced from the same lacquer systems by other deposition procedures.

It has been established in a number of studies[55,56] that the lifetime of polymer coatings obeys the relation

$$t = A e^{-\beta x},$$

where t is the time before the breakdown of the coating, x a characteristic of the state of the coatings which may be a number which represents the estimated state of the coating, the disruptive or internal stresses, the change in the content of functional groups, etc., A = the logarithm of the time required for the attainment by the coating of the state estimated in terms of a specified number, and β is the rate of change of the state of the coating. Thus, in terms of logarithmic coordinates, there is a linear relation between $\lg t$ and x.

It follows from the data in Fig. 5 that the protective properties of the electrodeposited coating persist appreciably longer than those of the coating produced by spraying when tests are made for water resistance (Fig. 5*a*); in tests carried out in a salt mist chamber (Fig. 5*b*) the change in the properties of the coatings obtained by both electrodeposition and spraying begins simultaneously but the electrodeposited coatings lose their protective properties one and a half times more slowly than those produced by spraying[57].

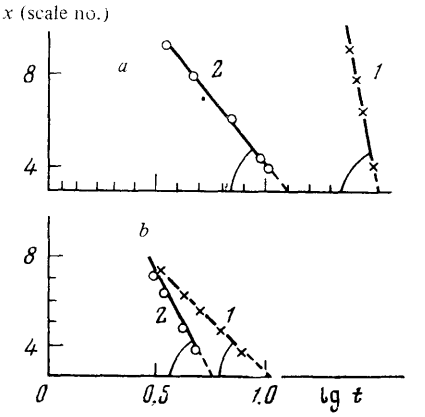


Figure 5. Variation in the state of the coatings based on the FL-093 primer deposited by electrodeposition (line *1*) and spraying (line *2*) in the course of ageing in a hydrostat (*a*) and in a salt mist chamber (*b*).[57]

(b) The influence of the nature of the metallic support. A characteristic feature of the coatings, which distinguishes them from other polymeric materials, is that they are formed on a support. The influence of the nature of the support on the structure and

properties of coatings produced by the methods based on solvent evaporation is determined both by the overall area of contact and by the shape of the surface, the number and nature of bonds at the boundary, and the nature of their distribution.

In oligomeric systems the formation of a structure inhomogeneous with respect to thickness and area takes place in consequence of the adsorption interaction of the oligomers with the support before the start of polymerisation. Furthermore, as shown above, in electrodeposition the nature of the support influences the chemical composition of the deposit formed on the anode.

It has been shown[58] that electrodeposition on steel and aluminium proceeds via a mechanism involving the formation of the acid form of the film-forming agent. The electrodeposition on aluminium is characterised by a lower degree of oxidation of the film-forming agent on the anode, as a result of which the oxygen evolved in the electrolysis of water is consumed to a greater extent on aluminium anodisation processes. Electrodeposition on copper involved the formation of the salt form of the film-forming agent. The above specific features of the formation of the electrodeposit on anodes of different kinds are responsible for the differences between their structural-mechanical properties (Table 2).

Table 2. The influence of the nature of the support on the conventional viscosity η of rezidrol electrodeposits and on the M_c for coatings formed on different metals[58].

Metal	$10^{-5}\eta$, Pa s	M_c at the hardening temperature			
		130°	180°	200°	225°
Copper	2.000	157	76	49	25
Steel	0.480	184	98	87	69
Aluminium	0.324	374	280	241	225

The conventional viscosity of the deposit, calculated from the rate of development of the shear deformation between two plane-parallel plates, is a maximum for a copper support. The greater conventional viscosity of films on steel compared with aluminium can be accounted for by the greater degree of oxidation of the film-forming agent. During thermal hardening on steel and aluminium, the formation of a three-dimensional network in oils is associated with oxidative polymerisation.

In a coating on copper double bonds are retained even at 275°C. The cause of this is the blocking of the double bond by copper ions, which can form a coordinate bond with the latter. Nevertheless data obtained by the direct determination of the molecular weight of the section of the chain between the effective nodes of the three-dimensional network (M_c) showed that the greatest density of cross-links obtains in the coating electrodeposited on copper. These phenomena are associated with the fact that the mechanism of film formation in electrodeposition on copper is in principle different from that of film formation on steel and aluminium and consists in the formation of ionic and coordinate bonds with copper ions.

The results of the determination of the mechanical properties of the coatings during hardening agree satisfactorily with the film formation mechanism examined above[58]. Coatings obtained on steel and aluminium supports exhibit the greatest and smallest resistance to wear. The formation of a three-dimensional network on a copper support via ionic bonds is responsible for the higher resistance to wear of the coatings at a low hardening temperature and the smaller influence of the hardening temperature on the mechanical properties as compared with steel. The lower resistance to wear of the coatings on copper, compared with steel, at temperatures above 150°C is associated with their greater rigidity and their coarsely globular structure, which retard the relaxation processes.

III. THE MECHANISM OF THE ELECTRODEPOSITION OF THE PIGMENT COMPONENT OF WATER-MISCIBLE LACQUER MATERIALS

Apart from film-forming materials, the most important components of the lacquer system are pigments and fillers. However, the problem of the mechanism of the electrodeposition of filled systems containing water-soluble film-forming agents has been very little studied. Previously it was assumed that the electrodeposition of pigments obeys the rules governing the electrophoretic deposition of dispersions, although this was not confirmed experimentally. The existing ideas about the mechanism of the electrophoretic deposition of dispersions are applicable to lyophobic colloids stabilised by an ionic mechanism. They are based on Deryagin and Landau's theory of the stability and coagulation of lyophobic colloids, which at its present stage of development takes into account not only pair but also collective interactions of the species, the possibility of their fixation at long distances from one another, as well as the influence of homogeneous and inhomogeneous electric fields[59-68].

The systems of water-soluble lacquer materials considered here differ from the systems of lyophobic colloids stabilised by an ionic mechanism primarily by the fact that the concentration of the third component, constituting, together with the aqueous dispersion medium, a single phase, is very high compared with the concentration of the disperse phase. In fact, one is dealing with dispersions of pigments in a concentrated aqueous solution of a polyelectrolyte. The problems of the stability, electrokinetic properties, and electrodeposition of such systems have already been examined[69-72].

1. Interaction of Water-Soluble Film-Forming Agents with Pigments

Since in the absence of a film-forming agent there is no electrodeposition of the majority of pigments from a pigment–water system on electrodes[73,74], it was concluded that the pigment particles in an aqueous medium are surrounded by particles of the binder, which impart to them a negative charge[74-76] and are responsible for their electrodeposition[74-77].

The interaction of water-soluble film-forming agents with pigments was studied in relation to the Printex U carbon black and R-820 titanium dioxide, which are used in electrodeposition systems[69]. The determination of the ξ-potential of the particles and of the sedimentation potential on a Figurovskii balance demonstrated the stabilising influence of film-forming agents in relation to pigments. It has been established on the basis of the surface tension isotherm of an aqueous solution of rezidrol in the presence of pigments that a considerable degree of

adsorption is characteristic of the test systems. In order to determine its nature, a study was made by a gravimetric method of the adsorption of rezidrol on the test pigments from aqueous solutions at different concentrations with subsequent removal by washing; the results were used to calculate the adsorption parameters. It was established that part of the adsorbed film-forming agent is bound to the surface of the pigment by irreversible linkages. Thus in real electrodeposition systems the pigment is stabilised by a binder adsorbed on its surface. This condition is necessary for the electrodeposition of the pigment on the anode, which has been demonstrated by the absence of the electrodeposition of oxidised carbon black from an aqueous medium. In this case the carbon black–water system has a high kinetic stability and a high ξ-potential of the particles (62 mV); nevertheless in an electric field the carbon black particles are not deposited on the anode.

Thus the deposition of pigments on the anode is determined by the film-forming agent linked to their surface by adsorption interaction.

2. The Nature of the Stability of Dispersion of Pigments in Solutions of Water-Soluble Film-Forming Agents

In order to elucidate the nature of the stability of the systems under consideration, a study was made of their aggregative and kinetic stability as a function of the ξ-potential of their particles[69]; the ξ-potential was varied by introducing into the system a 20% NaCl solution, which influences the thickness of the electrical double layer but does not lead to the loss of solubility of the film-forming agent, and also by changing the pH of the medium within the limits where the film-forming agent is soluble. Despite the fact that the ξ-potential was changed almost by a factor of two, neither the optical density of the systems nor the volume and weight of the sedimentation deposit were changed. Consequently the aggregative and kinetic stabilities of the dispersions are not affected by a change in the ξ-potential.

The data quoted show that, apart from the ionic-electrostatic factor, the non-electrostatic stability factor plays an important role in the mechanism of the stabilisation of the particles. This is demonstrated by the finding that, when the concentration of the film-forming agent in solution diminishes appreciable (to a value less than that required for the complete adsorption saturation, calculated as 15 mg of rezidrol per gram of TiO_2), the ionic-electrostatic stability factor becomes of decisive importance in the stabilisation mechanism[67,71]. An analogous conclusion was also reached in a study[78] devoted to colloidal chemical interaction of titanium dioxide with water-soluble acrylic copolymers.

3. The Study of the Electrodeposition of Pigments on the Anode

The electrodeposition of pigments on the anode has been examined[71] in relation to the rezidrol–titanium dioxide system. The influence of the electrodeposition parameters on the variation of the amount of the electrodeposited pigment on the anode is analogous to the influence of the deposition parameters on the yield of the deposit on the anode for a non-pigmented solution of a film-forming agent, which indicates the decisive role of the latter in the pigment electrodeposition mechanism. The coagulation thresholds for the test systems of filled carboxyl-containing polyelectrolytes virtually correspond to the concentration of the precipitant causing the precipitation of a deposit from a solution of an unfilled film-forming agent.

However, there is also a weak variation of the yield of the pigment deposit on the anode with the ξ-potential of the particles. One may therefore conclude that electrophoresis may be important in the mechanism of the concentration of pigment particles in the layer near the anode. This factor explains the enrichment of the electrodeposited film in the pigment compared with the pigment concentration in the bath. An electrid field does not influence the optical densities of the systems; consequently, there is no structure formation in the test systems in an electric field. The dimensions of the pigment aggregates in the coatings obtained by the pouring and electrodeposition methods are the same. The attempt to apply quantitative electrophoretic relations to the calculation of the amount of electrodeposited pigment on the anode gave rise to more than an order of magnitude discrepancy between the experimental and calculated results.

Evidently the phenomena under consideration are caused by the fact that the non-electrostatic stability factor plays an appreciable role in the mechanism of the particle stabilisation in the test systems; consequently, the theory of the electrophoretic formation of deposits on the anode, developed for systems stabilised by an ionic mechanism, cannot be applied to the case under consideration[79]. The deposition of pigments on the anode is due to the loss of solubility in the anodic compartment by the water-soluble film forming-agent adsorbed on the surface of the pigments. On the other hand, if the stability of the dispersions is caused mainly by the electrostatic factor (the TiO_2–0.02% rezidrol solution system), structure formation does take place in an electric field. In this case the determination of the yield of the pigment on the anode as a function of the duration of the electrodeposition gives results closer to data calculated in accordance with the electrophoretic mechanism[71,72].

4. The Influence of Pigments on the Parameters of the Electrodeposition Process

There are data, albeit contradictory, showing that pigments can influence the thickness and the electrical resistance of the anodic deposit and hence also the electrodeposition parameters[74,80]. The influence of the Printex U carbon black and titanium dioxide (R-820) on the electrodeposition process has been studied at constant currents and potentials in relation to rezidrol[72]. The results were compared with the structural-mechanical properties of non-hardened coatings obtained from the rate of development of the shear deformation between two plane-parallel plates, and also with the viscosities and electrical conductivities of the systems used for electrodeposition. It was established that the influence of the pigments on the electrodeposition parameters depends on their influence on the rheological properties of the electrodeposited system and the resulting coatings and also on the ability of the pigments to form conducting structures in a system with a film-forming agent. Thus the data presented confirm the validity of the hypothesis that the electrodeposition of pigments on the anode takes place as a result of the loss of solubility, in the layer near

the anode, by the film-forming agent linked to the surface of the pigments by adsorption interaction.

IV. THE INFLUENCE OF ELECTRODEPOSITION CONDITIONS ON THE FORMATION OF A DEPOSIT ON THE ANODE AND THE PROPERTIES OF THE COATINGS

Apart from the composition of the lacquer system, the electrodeposition of water-soluble lacquer materials and the properties of the resulting coatings are known to be greatly influenced by the concentration and pH of the lacquer material in the bath, the electrical parameters, the process time, temperature, and rate of stirring[7,13,14,73,81]. The form of the rectified current has been found to have an influence in a number of investigations[82-84]. Coatings with optimum properties are produced in a specific range of values of the parameters enumerated. The causes of the influence of the deposition parameters on the electrodeposition process and the properties of the coatings have been investigated[85-87].

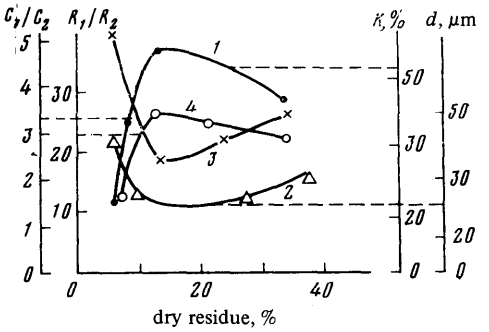


Figure 6. Dependence of the scattering capacity of the bath K (curve *1*), the thickness of the coatings d (curve *2*), and the ratios of the capacitative (C) (curve *3*) and ohmic (R) (curve *4*) components of the impedance obtained at frequencies of 500 Hz (R_1, C_1) and 20 000 Hz (R_2, C_2) on the rezidrol concentration in the bath[85].

1. The Influence of the Concentration of the Lacquer Material in the Bath

The dependence of the protective properties of coatings and of the scattering capacity of the bath on concentration is illustrated in Fig. 6. The maximum scattering capacity of the bath corresponds to the most effective corrosion-protective properties of the coatings characterised by the capacitative–ohmic method[88].

Electron microscope studies of the structure of the coatings showed that structural elements of smallest size are then close-packed to the maximum extent. At a rezidrol concentration smaller or greater than the optimum value, the coatings have a structure with loose packing.

It has been shown[85] that the influence of the concentration of the aqueous solution on the electrodeposition process and the structure and properties of the resulting coatings is associated with the difference between the supermolecular structures of the solutions of the film-forming agents. The study of the viscosities and conductivities of these solutions showed that at elevated concentrations, where the resistance of the anode diminishes, the protective properties of the coatings become less effective, and defects such as bulges arise, structure formation processes begin in the test solutions. This results in an increase of the mass of each structural element of the solution involved in the interaction with hydrogen ions, which leads to the formation of thickened coatings with bulges. Under these conditions, the number of carboxylate ions on the surface of each structural element involved in the neutralisation processes diminishes, as shown by the shift of the inflections on the conductimetric titration curves towards lower pH values. Under the conditions of a structured solution, the deposition of the same mass of polymer as at lower concentrations therefore requires a smaller number of hydrogen ions. This results in an increased acidity in the anodic compartment, which leads to an increase of the solubility of the anode, the expansion of the diffusion layer in the anodic compartment where deposition takes place, and the formation of thickened coatings with a loose packing of the structural elements.

If the electrodeposition is carried out in a structured solution with reduced electrical parameters (i.e. the concentration of hydrogen ions formed in the anodic compartment during the electrolysis of water is diminished), then it is possible to avoid the above defects to a large extent. In electrodeposition in the region of reduced concentrations of the film-forming agent in the anodic compartment there is apparently also an excess of free hydrogen ions owing to the low concentration of the ions of the film-forming agent. The reaction zone therefore expands, which results in the formation of loose bulky deposits and the solubility of the anode increases owing to the increased acidity of the solution in the anodic compartment.

The electrodeposition of low-resistance film-forming agents has characteristic features due to the poor structural-mechanical properties of their deposits. In the region of concentrations where structure formation takes place in the solution, a decrease and not an increase in the weight of the coating is observed during delectrodeposition. This is apparently caused by the slipping of the deposit from the anode under the influence of its own weight owing to its poor structural-mechanical properties. Such slipping can be observed visually. It entails the formation of bulges and runs on the coating.

2. The Influence of the Electrical Parameters and Process Time

With increase of the potential and current and also process time, an increase in the weight of the coating is initially observed in accordance with a virtually linear law, the growth of the thickness of the coating then slows down, and, on further increase of the electrical parameters and process time beyond certain limiting values, "superdeposition" defects are observed on the coatings, manifested by bulges and a "shagreen" effect; for low-resistance lacquer materials, a decrease in the weight increment of the coatings is observed.

The maximum packing density and the most effective protective properties of the coatings correspond to the optimum electrical parameters and process time. With increase of time, potential, and current above the optimum values, coatings are formed which consist of

aggregates of indefinite form and with a loose packing. Direct measurement of the temperature of the anode established[86] that the above phenomena are caused by the increased evolution of heat with increase of the above parameters. The decrease of the quality of the rezidrol coatings described above is observed when the temperature of the anode exceeds 60°C, the reaction time is 2 min, and the potential is 200 V. The impairment of the quality of the coatings is altogether absent in electrodeposition on a cooled anode whose temperature does not exceed 30°C, at a potential up to 300 V, and for a process time up to 5 min. It has been shown that, with increase of the temperature of the anode, there is an appreciable increase of the rate of formation of a deposit on the latter, which impairs the structure and protective properties of the coatings.

In the electrodeposition of low-resistance lacquer materials an increase of the electrical parameters and process time entails an increase of the rate of electrodeposition and of the thickness of the coatings, which is followed by their decrease owing to the poor structural-mechanical properties of the deposits, the latter becoming still more inferior when the temperature increases.

3. The Degree of Neutralisation of the Binder and the Type of Neutraliser

The solubility in water of film-forming agents used for electrodeposition is ensured by the neutralisation of carboxy-groups by bases. Electrodeposition takes place in an alkaline medium. The pH of the lacquer material has a significant influence on the stability of the lacquer system, the rate of electrodeposition, and the quality of the coatings in electrodeposition. As a rule, for each lacquer material there is an optimum pH range. The existence of a lower pH limit is due to the stability of the water-soluble film forming-agents whose acid form is insoluble in water. An increase of pH entails an increased degree of neutralisation of the carboxy-groups of the film-forming agent and an increase in the charge per unit molecular weight (owing to the increase of the degree of dissociation). This is accompanied by an increased repulsion of like charges and an increased solubility of the film-forming agent in water. In a highly alkaline medium an aqueous system is so stable that the formation of coatings by electrodeposition is hindered[73,77,81].

The thickness of the electrodeposition coatings therefore increases with increasing pH of the system and the curve relating the scattering capacity of the solution in the bath and the protective properties of the coatings to the pH passes through a maximum. The presence of the latter is caused, on the one hand, by the decrease of the size of the structural elements of the solution with increasing pH and by the increase of the packing density in the structure of the coatings and, on the other hand, by a significant decrease of the thickness of the coatings.

There is information showing that not only the pH but also the type of neutraliser used to convert the film-forming agent into a water-soluble state can influence the electrodeposition process[89-92]. In order to render the film-forming agent water-soluble, different neutralisers are employed: ammonia, primary, secondary, and tertiary alkylamines, hydroxyalkylamines (aminoalcohols), and morpholine; inorganic alkalies (KOH, NaOH) are sometimes used. The influence of the type of neutraliser on the electrodeposition process has been investigated[93] in relation to rezidrol. The following neutralisers were used: ammonia, triethylamine (TEA), triethanolamine (TEOLA), and diethylenetriamine (DETA). It was established that, in the neutralisation of polyacids by diethylenetriamine, conformational transformations take place in the system, associated with the partial "twisting" of the macromolecules and with processes involving partial conversion into a globular form. The reason is that the composition of DETA includes two primary amino-groups and one secondary amino-group. As a result, the film-forming agent forms amide linkages with two primary DETA amino-groups and the remaining free carboxy-groups interact with the secondary amino-groups of the neutraliser. The coatings formed in electrodeposition from globular solutions exhibit a reduced capacity for relaxation processes. Consequently, owing to the increase in the polarisation component, there is an appreciable increase of the resistance of the anode, which permits electrodeposition at higher potentials. As a result, DETA can be recommended as an additive to the electrodeposition bath in order to increase the potential, which makes it possible to increase the scattering capacity of the bath[94].

4. The Influence of Deposition Parameters on the Physicomechanical Properties of the Coatings and the Molecular Weight of the Section of the Chain between the Effective Nodes of the Three-Dimensional Network

The influence of the above electrodeposition parameters on the physicomechanical properties of coatings and the quantity M_c has been studied[95] in relation to rezidrol. In order to estimate the physicomechanical properties of the coatings as a function of the deposition conditions, a generalised parameter, namely the resistance to wear, was adopted as a criterion. The rupturing force for coatings electrodeposited on aluminium foil was also determined as a function of the deposition parameters—from the difference between the strength of the coating—foil system and the strength of the foil without the coating. It was established that coatings with the optimum mechanical properties are formed for the same electrodeposition parameters as in the formation of coatings with the optimum protective properties and with the maximum scattering capacity of the system, i.e. under conditions where the formation of a coating whose structure consists of elements of the smallest size is most uniform and is most close-packed. At the same time, M_c (according to equilibrium swelling data) for coatings formed for different electrodeposition parameters changes only slightly, but the minimum value of M_c corresponds to the coating produced for the optimum parameters. All these findings suggest that, as the electrodeposition parameters are changed, the chemical bonds within and between structural elements of the coating are redistributed.

5. The Influence of Hydrodynamic Conditions in the Bath on the Electrodeposition Process

The electrodeposition of water-miscible lacquer materials takes place with constant stirring whose optimum rate depends primarily on the lacquer material employed; usually the optimum rate of stirring is chosen empirically. There are data[24-26,96,97] showing that the hydrodynamic conditions in the bath (i.e. the rate of stirring) influence the thickness of the electrodeposited coating. It has been shown[24] in relation to the electrodeposition of acrylic

lacquer on a rotating disc electrode that there is a definite (limiting) rate of rotation of the disc electrode above which a deposit is not formed. The authors explain this phenomenon by the decreased thickness of the diffuse component of the electrical double layer and hence by the decreased number of hydrogen ions required for the formation of a deposit.

The influence of the rate of stirring of the lacquer material on the rate of electrodeposition, the thickness and protective properties of coatings, and the relation between the rate of stirring and the electrodeposition parameters has been investigated[7] for the FL-093 primer and the FL-149E enamel. For both lacquer materials, there is a sharp decrease of the rate of electrodeposition with increasing rate of stirring and its extent is the same. This is because, with increase of the rate of stirring, there is the same decrease in the thickness of the diffuse layer of hydrogen ions produced in the electrolysis of water and responsible for the formation of the deposit. However, the maximum rate of stirring at which the coating is not formed is higher for the FL-093 primer, which is probably associated with the higher conventional current yield, i.e. with the higher rate of the electrodeposition in the absence of stirring compared with the FL-149E enamel. The increase of the optimum range of electrical parameters and of the deposition time with increasing rate of stirring has been established by the capacitative-optical method. Direct measurement of the temperature of the anode by means of a Chromel–Copel thermocouple showed that this is caused by the decreased temperature of the anode with increasing rate of stirring, which is related to the influence of the rate of stirring on the heat transfer in the system.

Since the scattering capacity of the bath in colouring by electrodeposition is proportional to electrical parameters, it can be increased by creating a special stirring system in the bath.

6. The Influence of the Pulsation of the Rectified Current on the Electrodeposition Process

The electrodeposition of water-miscible lacquer materials requires the use of a rectified current. The coloured layers obtained at a constant potential and at a constant current density are distinguished in terms of the mode of supply of the electric current. There have been a number of studies and patents[82–84, 98, 99] devoted to the problems of the selection of schemes for the supply of the electric current in electrodeposition. In particular, there is information showing that with a pulsed supply of the current an increase in the thickness of the electrodeposited coatings is observed in some cases[98]. The influence of the form of the rectified current on the electrodeposition process under the conditions of a constant potential has been investigated[86]. It has been established that the influence is associated with the differences in the thermal phenomena on the anode when different schemes for the rectification of the current are used. An increase of the amplitude of the pulsations for the same effective rectified current leads to greater heating of the anode largely owing to the change of the maximum rectified current. In the single-phase half-wave rectification, a current passes through the bath during one half-period, its amplitude exceeding almost by a factor of three the effective value. This probably leads to an increase of the amount of heat evolved during a time shorter than one half-period. Owing to the low thermal conductivity of the film, the heat evolved gradually accumulates in the deposited layer and the temperature of the anode continues to increase. The increase of the temperature of the anode increases the rate of electrodeposition. This results in the formation of thicker coatings (or, in the case of low-resistance lacquer materials, thinner coatings owing to the slipping of the film from the anode because of its poor structural-mechanical properties), but the scattering capacity of the bath decreases and the protective properties of the coatings become less effective. Hence the pulsed supply of the current is desirable only in the electrodeposition of film-forming agents with a high rigidity.

Thus the mechanism of the process involving the formation of polymer coatings, developed in the last 10–15 years[100–104], operates also in the formation of films from water-miscible lacquer materials by electrodeposition. Under these conditions, the polymer coating is produced from the structure arising in the anodic compartment before the start of the thermal hardening process when the oligomer loses its solubility in water; the deposit is formed on the anode owing to the interaction with the hydrogen or metal ions formed as a result of the accompanying electrochemical reactions in the aqueous medium at the anode.

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Transformations in Refractory Compounds, Brought about by High Pressures and Temperatures

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The influence of high pressures and temperatures on the structural characteristics of the refractory carbides, nitrides, and monoxides of the transition metals have been examined. The results have been discussed in the light of one of the components of Kurnakov's theory of daltonides and berthollides—the concept of imaginary compounds, developed by Bokii. A number of new ideas following from this examination have been formulated. It has been shown that at high pressures and temperatures it is possible to obtain new electronic modifications of compounds and to extend considerably the range of existence of phases of variable composition. It has been shown that the concept of imaginary compounds is correct, and it has been suggested that a large number of imaginary compounds are realised at high pressures and temperatures. Other methods of obtaining imaginary compounds have been recommended. The bibliography contains 109 references.

CONTENTS

I.	Introduction	1225
II.	Carbides	1225
III.	Nitrides	1228
IV.	Monoxides	1228
V.	Oxide carbides and oxide nitrides	1230
VI.	Summary	1230

I. INTRODUCTION

In recent years there has been considerable interest in the study of processes taking place in a solid under the simultaneous influence of high pressures (p) and temperatures (t). This is due because it is thus possible to bring about various transformations (polymorphic transformations, decomposition and reduction of a substance, perfection and ordering of a crystal structure, transitions from the crystalline state to the amorphous and vitreous states, production of the metallic state, changes in the electronic structure of compounds and the valency state of atoms, the synthesis of periodic and "imaginary" compounds, the production of new electronic modifications of known compounds, etc.); see for example Refs. 1–34.

In the present work an attempt is made to examine systematically the influence of high p and t chiefly on refractory carbides and nitrides and partly on oxides of the transition metals and their reciprocal solid solutions.

The compounds discussed, which are formed chiefly from metals of sub-groups IVa–Va, belong to the class of so-called interstitial phases and are distinguished by a number of characteristic features, which it is appropriate to discuss briefly. Firstly, most of these compounds (which exhibit the properties of metals or covalent crystals) have wide homogeneity ranges, and their unit cells sometimes contain a large number of structural vacancies in one part (for example the monocarbides of the transition metals of groups IV and V, and Fe monoxide) or both parts (for example the cubic NaCl-type monoxides of Ti and V, and the oxide carbides and oxide nitrides of Ti, Zr, Hf, V, and Nb). The metal atoms of these compounds often exhibit cubic or hexagonal close packing, with the non-metal atoms arranged in the octahedral sites. Under certain conditions, some interstitial phase compositions exhibit ordering ($NbC_{0.75}$, $TaC_{0.75}$, $TiO_{1.00}$, $TiC_{0.5}O_{0.5}$, $VC_{0.5}O_{0.5}$, etc.). More detailed data on interstitial phases are given in a number of monographs (see for example Refs. 35–38).

II. CARBIDES

The first report of the influence of high pressures† on carbides, including those of refractory metals, is found in papers dealing with the synthesis of artificial diamonds. In these papers (reviewed, for example, in Refs. 2, 23, and 40), carbides are used as the carbon-containing material, which liberates carbon at high p and t as a result of chemical reactions.

The first special study of the influence of high pressures on the refractory carbide (and nitride) of titanium TiC (and TiN), of unknown composition, was carried out by Bridgman[40], who determined the compressibility and electrical resistance at a pressure $p = 1.2 \times 10^4$ kg cm^{-2} and found that the electrical resistance decreased with increase in pressure; no structural transformations were recorded. Semerchan and coworkers[41] studied the influence of pressure (up to 10^5 kg cm^{-2}) and temperature (1400°) on the hard alloy T15K6 (composition, wt.%: Ti 12.5, C 7.5, Co 6.0, Fe 0.1, remainder W). The specimens in the form of cylinders of diameter 6 mm and height 8 mm were kept under these conditions for 5 min in the apparatus previously developed[42]. The heating was then stopped, and when the temperature had decreased to ambient the pressure was also removed. The alloy treated in this way consisted of three phases—the carbide WC, a solid solution of tungsten carbide in titanium carbide TiC–WC, and a solid solution of tungsten (up to 3%), titanium (up to 0.5%), and carbon (up to 0.5%) in cobalt, Co(W, Ti, C). (Semerchan and coworkers[41] report that the loss of carbon by the specimens during this treatment was prevented, but they do not describe how this was achieved.) The experimental data are given in Table 1.[41] The decrease in the specific gravity of the treated specimens compared with the original specimens

† In accordance with the published classification[39], high pressures correspond to $p \geq 10^4$ kg cm^{-2}.

was attributed[41] to the filling of the cracks by katlinite—the medium in direct contact with the specimen, used to transmit the pressure. The decrease in the lattice spacing of the phase TiC–WC is related to the additional solution (up to 5 wt.%) of WC in TiC. In the X-ray diffraction patterns of the treated alloy, the diffraction maxima were broader, and their point character, observed for the original specimen, had disappeared. All this was attributed[41] to the production of distortions in the crystal structure of the carbide phases.

Table 1. Influence of high pressure and temperature on the characteristics of the alloy T15K6.[41]

Characteristics of the specimens	Original alloy	Treated alloy
Specific gravity, g cm^{-3}	11.25	11.0–11.48
Average particle size of the phase WC, μm	3.46	3.65
Average particle size of the phase TiC–WC, μm	3.60	3.56
Concentration of graphite inclusions in the field of view, %	up to 0.5	up to 0.5
Porosity, %	up to 0.2	up to 0.2
Vickers hardness, kg cm^{-2}	1480	1480–1100
Lattice period of the phase TiC–WC, A	4.3119	4.3105
Width of the 420 diffraction line of the phase TiC, min	63	92
Width of the 202 diffraction line of the phase WC, min	80	153

Pivovarov and coworkers[43] subjected specimens of the hexagonal carbide $WC_{0.99}$ to all-round compression (up to ~100 kbar) with simultaneous heating (up to 2130°C). Under these conditions, the diffraction maxima became appreciably broader (the width of the 211 line increased from 6 mradian to 26 mradian). Moreover, this treatment led to a significant increase in the micro-hardness (from 1800 kg mm^{-2} to 2800–3200 kg mm^{-2}). These results were attributed to an increase in the density of dislocations and other defects in the crystal lattice, leading to plastic deformation of the carbide $WC_{0.99}$.[43] When the specimen was annealed to 1800° for 1.5 h, the micro-hardness decreased to 1870 kg mm^{-2}; at the same time, the width of the diffraction line decreased to 14 mradian. The same effects were observed by Koval'skii and coworkers[44], when the carbides WC, TaC, TiC, NbC, ZrC, and Cr_3C_2 were treated for 3 min under conditions of quasi-hydrostatic pressure (p = 100 kbar) with simultaneous heating to 1400°; part of the carbides contained up to 3 wt.% cobalt. These data[44] are given in Table 2. Koval'skii and coworkers[44] also drew attention to the marked increase in the micro-hardness and the broadening of the X-ray lines after treatment. In this case, in contrast to the earlier data[43], annealing did not lead to a significant change in the micro-hardness of pure tungsten carbide (the conditions of annealing, however, were slightly different from those described in Ref. 43, see Table 2). The addition of cobalt leads to a marked increase in the rate at which the hardness decreases, as a consequence of the participation of the liquid phase in the recrystallisation (see Table 2), including that in WC.

Unlike Koval'skii and coworkers[44], Samsonov and coworkers[45] were able to achieve a significant increase in the micro-hardness of specimens of titanium carbide TiC treated under conditions of quasi-hydrostatic pressure in the range 25–80 kbar and temperatures in the range 1000–2000°. The specimens were first heated in cells to the required temperature, kept at this temperature for 3 min, and then compressed for 1 min. The maximum micro-hardness achieved in the compressed titanium carbide[45] was 3300 kg mm^{-2}.

Table 2. Characteristics of the alloys studied by Koval'skii and coworkers[44].

Parameters	Original specimens								
	TiC+Co	ZrC	NbC+Co	NbC	TiC+Co	WC+Co	VC	Cr_3C_2+Co	Cr_3C_2
Micro-hardness, kg mm^{-2}:									
original specimen	2400	2900	1800	1800	1600	1800	1800	1350	1350
treated specimen	2500	2900	2600	2600	2200	3100	3100	2600	2600
after annealing*	2400	3000	1800	2100	1700	1900	3000	1700	2200
Broadening of the lines, radian	8.75×10^{-4}	1.75×10^{-3}	1.31×10^{-2}	1.16×10^{-2}	1.05×10^{-2}	1.13×10^{-2}	2.33×10^{-3}	9.35×10^{-3}	8.20×10^{-3}

* Annealed at 1400° for 3 h.

Samsonov and coworkers[46] applied static and dynamic pressures to specimens of hexagonal tungsten carbide WC_X (x = 0.85, 0.90, 0.95) and mixtures of the metal and carbon black with the same compositions. Shock compression was applied in retaining ampoules; the pressure at the front of the leading wave was $(1.45–1.65)\times10^6$ kg cm^{-2}. The quasi-hydrostatic pressure treatment was carried out at 1200° and 90 kbar for 30 min. X-Ray phase analysis and measurement of the micro-hardness of the specimens treated in this way revealed individual granules and conglomerates of granules of the cubic modification of WC.[46] The formation of the cubic carbide WC was observed on compression of both the original carbides ($WC_{0.90}$ and $WC_{0.95}$) and the mixtures of tungsten and carbon black having the same compositions. Explosive shocks[46] also led to decomposition of the original hexagonal carbide $WC_{0.95}$ to metallic tungsten, hexagonal W_2C and cubic WC. An interesting feature is that it has been reported[47] that high-temperature cubic WC, synthesised under ordinary conditions, has a restricted range of existence with respect to both composition ($WC_{0.61-0.67}$) and temperature (2530–2747°).

Sevast'yanova and coworkers[48] synthesised cubic tungsten carbide under conditions slightly different from those used by Samsonov and coworkers[46]. Hexagonal tungsten carbide and a mixture of finely divided metallic tungsten and carbon black in equi-atomic proportions were subjected to high pressures (35–70 kbar) and temperatures (1400–2000°). The duration of treatment was varied from 1 min to 3 min. In addition, the original specimens contained 0.1–2 at.% of stabilisers—metals of groups IV and V and their cubic carbides TiC, ZrC, and VC. When hexagonal tungsten carbide was used as starting material, the cubic carbide could not be obtained, even when stabilisers were added. It was formed, however, by compressing a mixture of the metal and carbon black containing TiC. The lattice period of the cubic phase, determined from the 220 line for one of the heterophase specimens, was 4.336 Å. This large value of the lattice period was attributed to the formation of a solid solution WC–TiC.

Clougherty and coworkers[49] treated an equi-atomic mixture of metallic molybdenum and carbon, and also Mo_2C and carbon, at high temperatures (1800–2500°) and pressures (40–70 kbar). X-Ray phase analysis of the resulting specimens showed the presence of ten additional lines, in addition to those of the phases existing under ordinary conditions. All were indexed in a cubic face-centred lattice with period $a = 4.27$ Å. This carbide was assigned the stoichiometric composition MoC, with four metal atoms in the unit cell[49]. Cubic molybdenum carbide synthesised under ordinary conditions exists in a different composition range ($MoC_{0.66-0.76}$) at temperatures of 1960–2600°.[50,51]

Table 3. Characteristics of MoC_x specimens[52].

Compn. of original specimen	Phase compn. of original specimen	Phase compn. after treatment* (lattice periods of individual components)
$MoC_{0.567}$	$Mo_2C + \eta$-MoC_x (hexagonal)	$Mo_2C + \eta$-MoC_x ($a = 3.02$ Å; $c = 14.41$ Å)
$MoC_{0.661}$	$Mo_2C + C$	η-$MoC_x + Mo_2C$
$MoC_{0.661}$	$Mo + C$	η-$MoC_x + Mo_2C$
$MoC_{0.733}$	α-MoC_x (cubic)	η-MoC_x ($a = 3.011$ Å; $c = 14.63$ Å)
	η-MoC_x (hexagonal)	α-MoC_x

* Treatment at 25 kbar and 1500° for 14 min.

Table 4. Characteristics of specimens obtained by Dubrovskaya and Nazarova[53].

Original specimens				Treated specimens ($p = 120$ kbar, $t = 1500°$, $\tau = 30$ min)			
compn. of mixture	concentration of carbon, wt.%		a, Å	concentration of carbon, wt.%		a, Å	concn. of nitrogen, wt.%
	combined	free		combined	free		
$Nb_{0.95}Mo_{0.05}C$	11.0	0.28	4.4646	—	нет	4.4674	0.1
$Nb_{0.85}Mo_{0.15}C$	10.73	0.60	4.4528	10.38	0.17	4.4420	—
$Nb_{0.71}Mo_{0.29}C$	10.62	0.95	4.430	9.59	0.02 0.63	4.4341 4.4344	—
$Nb_{0.51}Mo_{0.49}C$	9.63	1.57	4.3926	9.68 8.88	1.02 1.22	4.3926 4.3897	—
$Nb_{0.30}Mo_{0.70}C$	8.90	1.64	4.3417	—	0.88	4.3629	—
$Nb_{0.15}Mo_{0.85}C$	7.94	2.42	4.295	—	1.01	4.319 4.3273	—

The behaviour of the carbide phases in the Mo–C system at high pressures was also studied by Shinyaev and coworkers[52]; heterophase alloys of molybdenum and carbon, and their mixtures having the composition $MoC_{0.661}$, were treated for 40 min at 25 kbar and 1500° in an apparatus of the "anvil with indentation" type (see Table 3). X-Ray diffraction study after treatment showed that all the specimens contained the hexagonal η-carbide. Its lattice periods in the specimen having the composition $MoC_{0.567}$ differed considerably from those of the carbide synthesised under ordinary conditions ($a = 3.006–3.011$ Å; $c = 14.61–14.64$ Å).[50,51] It was concluded[52] that the homogeneity range of η-MoC_x is extended towards lower concentrations of carbon at high p and t. In addition, a thermodynamic calculation[52] showed that a pressure of 25 kbar lowers the decomposition temperature of the hexagonal η-carbide from 1650° to 1380°.

Dubrovskaya and Nazarova[53] tried to achieve additional introduction of carbon into the lattice of the solid solutions $NbC_{1.0}$–$MoC_{0.67}$ to obtain specimens having compositions close to the stoichiometric. Mixtures of the solid solutions and free carbon were treated at a pressure of 120 kbar and 1500° for 30 min. Chemical analysis of these specimens showed a decrease in the concentrations of both free and combined carbon. An interesting feature is that the lattice period, compared with the original value, remained unchanged for one of the specimens, decreased for another, and increased for the remainder (see Table 4).

The all-round compression of a substance can also be brought about under dynamic conditions. Compression by explosion leads to various transformation in a solid[10,11,13,15,17,20,24,27,54]. The influence of pressure pulses on refractory compounds has been studied by a number of workers[55–60,62]. Appreciable micro-porosity has been reported[55] in various specimens subjected to compression by explosion, including TiC, ZrC, NbC, and WC. The X-ray diffraction patterns (particularly those of the ZrC, NbC and WC specimens show diffuse broadening of the lines, indicating that the crystal structure is imperfect. In addition to the lines due to the original phases the X-ray diffraction patterns of the carbides ZrC, NbC, and WC, recorded after compression by explosion[55], contained extra reflections (in the case of WC these lines belong to hexagonal α-W_2C), the intensity of which increased with increased strength of the shock wave. It was concluded[55] that partial decomposition of the carbides NbC, ZrC, and WC takes place. The X-ray density of the compressed specimens remained unchanged[55].

The increase in the strength of the hard alloy WC–Co (15 wt.% Co) under the influence of an explosion (pressure 105–230 kbar) has been studied[56]. The micro-hardness of the original alloy (1200–1365 kg mm^{-2}) and the carbide (1824–1994 kg mm^{-2}) increased sharply after compression: to 2173–2311 kg mm^{-2} for the alloy, and to 2954–3200 kg mm^{-2} for tungsten carbide. These results show satisfactory agreement with results obtained by other workers[44]. The density of the alloy increased[56] from 13.6 g cm^{-3} to 14.5 g cm^{-3}, and the tungsten carbide particle size decreased. A phase transformation in metallic cobalt from the hexagonal to the cubic modification was also observed[56].

The influence of dynamic compression (67–190 kbar) on the structure of the carbides of titanium (TiC_x; $x = 0.62$, 0.75, 0.83, 0.98), zirconium (ZrC_x; $x = 0.62$, 0.72, 0.80, 0.96), and niobium (NbC_x; $x = 0.72$, 0.82, 0.90, 0.99) in their ranges of existence has been studied[57]. The compression was carried out in cylindrical and annular retention ampoules. Hexagen, pentaerythritol tetranitrate, and fused trinitrotoluene were used as explosives. The X-ray diffraction patterns of the carbides, recorded after shock compression, showed broadening of the diffraction maxima[57]. In addition, some of the specimens showed an increase in micro-hardness (by 6.8% for $TiC_{0.62}$, 20% for $NbC_{0.72}$, 14.3% for $NbC_{0.82}$, 11.1% for $NbC_{0.9}$, and 11.6% for $NbC_{0.90}$) after the effect of the explosion. This indicated[57] the passage of plastic deformation in local volumes, which was also related to the increased density of dislocations in the compressed specimens.

The influence of shock waves (160–350 kbar) on the physicochemical characteristics of technical zirconium carbide (Zr 87.75%, $C_{combined}$ 10.15%, C_{free} 0.1%, Fe 0.35%, Mg 0.01%) has been studied[58]. The dimensions of the regions of coherent scattering, the degree of distortion of the crystal lattice, the pyknometric density, and other characteristics of both the original and the compressed specimens were determined. The pyknometric density remained unchanged (6.45 g cm^{-3}) up to a pressure of 160 kbar, then increased to a maximum (6.51 g cm^{-3}) at 160 kbar, and finally decreased up to a pressure in the shock front equal to 350 kabr, reaching a minimum value (6.37 g cm^{-3}). The lattice period of the phase remained unchanged at $a = 4.688 \pm 0.002$ Å. The increase in the pyknometric density was attributed[58] to a decrease in the concentration of defects as a result of the "collapse" of micro-cracks and micro-cavities.

The influence of pressure pulses on the carbides of chromium (850 kbar) and molybdenum (1.05 Mbar) has been studied[59]. In one of the original heterophase specimens containing Cr_7C_3 and Cr_3C_2, the explosion led to rupture of the ampoule. X-Ray phase analysis of the products showed the presence of the higher carbide $Cr_{23}C_6$ in addition to the original phases. The carbide Mo_2C, however, decomposed to Mo and α-MoC_x on compression. These results were attributed to a change in the electronic structure of the original phases under the influence of high pressures.

III. NITRIDES

There is very little published information on the influence of all-round compression on refractory nitrides. The effect of shock waves on the nitrides of niobium, zirconium, silicon, chromium, and gallium has been studied[60]. Cylindrical steel retention ampoules were used, and the explosive was hexagen. The nitrides of Zr and Si did not show structural transformations[60], but the crystal structure of chromium nitride became less perfect; gallium nitride decomposed. Under the influence of the shock wave, the original hexagonal nitride $NbN_{0.98\pm0.03}$ was converted into the cubic nitride δ-$NbN_{0.83\pm0.10}$ with lattice period 4.39 ± 0.01 Å and density 7.20 ± 0.01 g cm^{-3} (density of the original niobium nitride 7.932 ± 0.006 g cm^{-3}). This change in density was attributed to latent micro-porosity in the $NbN_{0.83}$ subjected to shock compression[60].

Cubic (NaCl type) tantalum nitride with lattice period $a = 4.358 \pm 0.001$ Å has been synthesised[61] at $p = 30$–100 kbar and $t = 1800°$. This nitride is fairly stable: the polymorphic transformation to a phase having the WC structure, stable under ordinary experimental conditions, took place only after heating for 4 h in a vacuum (10^{-5} mmHg) at 1200°. It was assumed[61] that the composition of the nitride obtained differs from the stoichiometric composition, since the temperature of its conversion into the superconducting state ($T_c = 6.5$ K) is lower than that for tantalum carbide, whereas in the isomorphous niobium carbide and nitride the opposite T_c ratio is observed: 17.3K for NbN and 11.0 K for NbC.[61]

Samsonov and coworkers[62] applied dynamic pressure (~ 3 Mbar) to powdered hexagonal stoichiometric tantalum nitride ($TaN_{1.0}$) and detected a cubic (NaCl type) phase with $a = 4.33$ Å in addition to the hexagonal phase. Samsonov and coworkers assigned to it the composition $Ta_{0.8}N(TaN_{1.25})$ and reported the presence of vacant sites in the metallic sublattice ($\rho_{expt} = 15.652$ g cm^{-3}) although this does not follow from the original data (calculation gives the values of 3.85 and 4.81 for the numbers of tantalum and nitrogen atoms respectively).

The action of high pressures (up to 80 kbar) and temperatures (up to 2000°) does not lead to structural changes in the nitride VN or in mixtures of the nitrides TaN and Ta_2N.[63]

IV. MONOXIDES

Before examining published data on the influence of high p and t on the monoxides TiO_x and VO_x, titanium oxide carbides and oxide nitrides, and iron monoxide, it should be noted that all these phases exhibit appreciable homogeneity ranges and have structural vacancies in both sublattices (only FeO_x has vacancies confined to the metal sublattice); see for example Refs. 35–38.

Table 5. Change in the lattice periods, density, and percentage of vacancies in $TiO_{1.0}$ with change in pressure and temperature[67].

Pressure	Temperature (°C) and conditions of preparation	Lattice period at 25°C, A	Density, measured at 25°C, g cm^{-3}	Concn. of vacancies, %	No. of atoms in the cell	
					n_{Ti}	n_O
1 bar	1725 (original specimen)	4.1784	4.97	14.0	3.42	3.42
1 bar	1500 (2 d)	4.1796	4.97	14.4	3.42	3.42
1 bar	1500 (2 d) + 1200 (3 d)	4.1812	—	—	—	—
1 bar	1100	4.1817	—	—	—	—
9.4 kbar	1100	4.183	—	—	—	—
30.2 kbar	1100	4.1907	—	—	—	—
36.3 kbar	110	4.1922	5.01	12.9	3.47	3.47
1 bar	1320	4.1805	—	—	—	—
15 kbar	1320	4.1862	5.03	13.0	3.48	3.48
39.3 kbar	1320	4.1938	—	—	—	—
56.4 kbar	1320	4.2013	—	—	—	—
77.4 kbar	1550	4.2064	5.68	0.0	3.99	3.99
1 bar	1650	4.1788	—	—	—	—
20.9 kbar	1650	4.1877	5.01	13.2	3.47	3.47
27.4 kbar	1650	4.1916	5.04	12.4	3.50	3.50
35.0 kbar	1650	4.1945	—	—	—	—
56.4 kbar	1650	4.2025	—	—	—	—
56.4 kbar	1650	4.2020	—	—	—	—
61.6 kbar	1650	4.2045	—	—	—	—
66.2 kbar	1650	4.2038	5.37	5.88	3.76	3.76
77.4 kbar	1650	4.2062	5.69	0.0	3.99	3.99

The decomposition of iron(II) oxide under the influence of hydrostatic pressure (10^4 kg cm^{-2}) has been studied[64]. The original FeO specimen with $a = 4.294$ Å was subjected to pressure and isothermal heating at 400, 450, 480, 500, 550, and 590°C. The products of the decomposition of wüstite ($aFeO \xrightarrow{p,t} bFe + cFe_3O_4 + dFeO$), obtained under pressure, contain much larger quantities of the metallic phase than specimens prepared without using high pressure (other conditions being the same).[64] The explanation given for this difference[64] is that in the first case the iron ions may partly fill the vacancies in the metal sublattice of FeO (since pressure generally decreases the rate of diffusion processes), forming chiefly the metallic phase. This was proved[64] by X-ray diffraction, magnetic measurements, metallography, and chemical analysis. The synthesis of stoichiometric wüstite $FeO_{1.00}$ by the reaction between $Fe_{0.95}O$ and Fe at high pressures (> 36 kbar) and temperature (770°) has been reported[65].

The simultaneous influence of high pressure (up to 78.1 kbar) and temperature (from 880° to 1650°) on the monoxide $TiO_{1.00}$ (a_{init} = 4.1784 Å and 4.1796 Å) has been studied[66,67]. At a pressure of 77.4 kbar and temperatures of 1550° and 1650°, the unit cell of this phase became complete (that is contained no structural vacancies). The gradual decrease in the concentration of vacancies with change in p and t [67] is shown in Table 5. The number of atoms in the unit cell was determined[67] from data on the composition and lattice periods, and from the density of the specimens, measured by flotation, hydrostatic weighing, and powder pyknometry. Table 5 shows that increase in pressure leads to a regular increase in the lattice period and density, and to a decrease in the number of vacancies.

With increase in pressure to ~60 kbar at room temperature[68], the lattice periods of specimens of non-stoichiometric $Ti_{0.82}$ and $TiO_{1.25}$ decrease. The same results were obtained for wüstite[69]. The authors cited[69], however, were not convinced that the vacancies were filled under the conditions of their experiment. In fact, calculations[69] showed that the disappearance of the vacancies, as observed in Ref. 67, should lead to an increase in a after treatment of the specimens, whereas the values of a for the monoxide specimens, including FeO, acquired practically their original value after the high pressure was removed.

The equilibrium concentration of structural vacancies in TiO at high pressures and temperatures has been calculated[70] by the methods of statistical thermodynamics. The calculations indicate that the concentration of vacancies decreases from 14.5% at a pressure of 1 bar to ~10–14% at 100 kbar.

Subsequent experiments[71,72] confirmed the chief results of the previous studies on the filling of the vacancies in titanium monoxide, and also gave new data. Specimens of TiO_x in the homogeneity range (x = 0.86–1.24) were subjected to all-round compression at p = 50–60 kbar and t = 1100–1300°.[71] This led to a considerable decrease in the number of vacancies in both sublattices of TiO_x (see Table 6). The same result was obtained[72] by treating specimens of $TiO_{0.88}$ and $TiO_{1.27}$ at p = 90 kbar and t = 500–1300°. The lattice periods of these specimens increased sharply compared with the original specimens (Table 7), and this was attributed to filling of the structural vacancies in the metal sublattice ($TiO_{0.88}$) and oxygen sublattice ($TiO_{1.27}$) to give complete lattices.

An interesting result was obtained by Zainulin and coworkers[72] who found that a specimen of $TiO_{1.27}$, synthesised at $t > 1300°$, consisted of three phases, unlike other specimens. Its X-ray diffraction pattern, in addition to the lines of the cubic monoxide with a = 4.230 Å, showed a phase with interplanar spacings close to those for orthorhombic TiO_2(II),[73] and tetragonal TiO_2. The latter was readily indexed in a structure of the rutile type with lattice periods a = 4.575 Å, c = 3.080 Å, c/a = 0.673. These values differ considerably from the values corresponding to rutile stable under ordinary conditions: a = 4.59373 Å, c = 2.95812 Å, c/a = 0.64395.[75] In the opinion of the authors cited[72], this indicates that at p = 90 kbar and $t > 1300°$, the $TiO_{1.27}$ specimen decomposes to TiO_2 and a Ti_2O phase having a lower oxygen content than $TiO_{0.88}$. In fact, according to Ehrlich[74], the lattice period (and the intensity ratio I_{111}/I_{200}) of the monoxide TiO_x obtained under ordinary conditions increases with decrease in the oxygen concentration over its homogeneity range. According to the data obtained by Zainulin and coworkers[72], $a(TiO_{0.88})$ (for p = 90 kbar and t = 1020° and 1200°) is smaller than the period of the cubic lattice in the two-phase specimen of $TiO_{1.27}$; the same applies to the ratio I_{111}/I_{200}.

Table 6. Influence of pressure and temperature on the structural characteristics of the phase TiO_x.[71]

x in TiO_x	Characteristics of the original TiO_x: density, g cm^{-3}	lattice period, A	number of atoms in cell: n_{Ti}	n_O	Conditions of experiment: p, kbar	t, °C	Characteristics of the compressed TiO_x: density, g cm^{-3}	lattice period, A	number of atoms in cell: n_{Ti}	n_O
0.86	5.057	4.189	3.63	3.12	60	1300	5.117	4.205	3.72	3.20
0.89	5.043	4.191	3.60	3.20	50	1100	5.162	4.200	3.71	3.30
0.90	5.029	4.190	3.58	3.22	60	1300	5.129	4.207	3.70	3.33
0.91	5.025	4.186	3.56	3.24	60	1300	5.083	4.203	3.64	3.31
0.95	5.054	4.185	3.52	3.34	50	1300	5.177	4.200	3.66	3.48
1.00	5.000	4.184	3.45	3.45	50	1300	5.058	4.200	3.54	3.54
1.01	4.984	4.181	3.43	3.47	60	1300	5.043	4.196	3.50	3.54
1.03	4.929	4.173	3.35	3.45	60	1300	5.064	4.200	3.51	3.62
1.06	4.975	4.174	3.36	3.56	60	1100	4.996	4.196	3.43	3.64
1.07	4.975	4.174	3.36	3.60	60	1300	5.032	4.193	3.44	3.68
1.10	4.947	4.178	3.32	3.65	60	1300	5.013	4.192	3.40	3.74
1.12	4.947	4.176	3.30	3.70	60	1300	5.000	4.190	3.37	3.78
1.13	4.921	4.173	3.27	3.70	60	1300	4.969	4.189	3.34	3.78
1.17	4.914	4.174	3.24	3.79	60	1300	4.963	4.188	3.30	3.86
1.18	4.907	4.173	3.22	3.80	60	1300	4.934	4.187	3.26	3.85
1.22	4.851	4.171	3.14	3.83	60	1300	4.942	4.182	3.23	3.94
1.24	4.870	4.170	3.14	3.90	50	1300	4.938	4.198	3.25	4.03

Table 7. Characteristics of the original specimens and the specimens obtained at a pressure of 90 kbar and different temperatures[72].

Compn. and characteristics of the original phase	t, °C	Duration of treatment, min	Phase compn. of compressed specimen	Type of lattice	Lattice period, A	No. of formula units (n) in cell
$TiO_{0.88}$; a=4.1890 Å; n=3.52	500	2	single-phase*	FCC*	4.189	—
ditto	1020	1	single-phase	FCC	4.2107	3.98
»	1200	2	single-phase	FCC	4.2170	4.01
$TiO_{1.27}$; a=4.1667 Å; n=3.06	720	3	single-phase	FCC	4.1742	3.15
ditto	1240	1	single-phase	FCC	4.1740	3.14
»	1300	2	three-phase	1) FCC	4.23	—
				2) tetragonal (rutile type)	a=4.575; c=3.080	—
				3) orthorhombic (α-PbO_2 type)	a=4.531; b=5.498; c=4.900	—

* The lines at large angles on the X-ray diffraction pattern are indistinct.
** Face-centred cubic.

Indirect evidence of the decomposition of the $TiO_{1.27}$ specimen was also obtained by Banus and coworkers[71], who obtained a very large cubic lattice period for a single-phase specimen of $TiO_{1.27}$ (see Table 6); this diverged considerably from the general $a = f(x)$ relationship. This value of a can probably be attributed to the decomposition of $TiO_{1.24}$ to TiO_x ($x \ll 1.24$) and TiO_2; because of the small quantities present, however, the presence of TiO_2 could not be detected by X-ray diffraction.

The influence of dynamic pressure on titanium monoxide has also been studied[76,77]. The following mixtures were subjected to shock compression[76] (p ~ 800 kbar,

$t \sim 1730°C$): $Ti + TiO_2 = 2TiO_{1.0}$; $2Ti + 3TiO2 = 5TiO_{1.2}$ $3Ti + 2TiO_2 = 5TiO_{0.8}$. The reaction products in all cases contained a cubic (NaCl type) phase with lattice periods equal to 4.177–4.179 Å, 4.169 Å, and 4.188 Å respectively. The subsequent action of shock waves on the monoxide synthesised in this way did not alter the lattice periods[76]. Similarly, no significant change in the concentration of structural vacancies was observed when $TiO_{0.84}$, $TiO_{1.06}$, and $TiO_{1.28}$ were subjected to shock compression at pressures up to 600 kbar.[77]

Table 8. Change in the structural characteristics of the vanadium monoxide phase under the influence of pressure p = 60 kbar and t = 1300°C.[78]

x in VO_x	Characteristics of the original VO_x				Characteristics of the original VO_x			
	density, g cm^{-3}	lattice period, A	number of atoms in cell		density, g cm^{-3}	lattice period, A	number of atoms in cell	
			n_V	n_O			n_V	n_O
0.86	5.736	4.034	3.506	3.015	5.816	4.043	3.589	3.087
0.88	5.752	4.039	3.515	3.093	5.797	4.054	3.579	3.150
0.94	5.677	4.053	3.451	3.244	5.732	4.066	3.518	3.307
0.96	5.674	4.058	3.445	3.307	5.751	4.068	3.518	3.377
0.99	5.602	4.068	3.401	3.367	5.650	5.084	3.471	3.436
1.02	5.583	4.077	3.388	3.456	5.658	4.086	3.456	3.525
1.09	5.507	4.099	3.340	3.641	5.581	4.104	3.349	3.650
1.15	5.419	4.120	3.292	3.786	5.458	4.124	3.326	3.825
1.20	5.371	4.130	3.249	3.899	5.402	4.133	3.275	3.930
1.23	5.329	4.133	3.209	3.947	5.374	4.133	3.236	3.980

Specimens of vanadium monoxide (a_{init} = 4.0738 Å) have been subjected to the simultaneous influence of high pressures (56.4 kbar) and temperatures (1650°).[67] An increase in the lattice period (due to the filling of vacancies) to 4.1004 Å and even 4.1295 Å was observed[67]. A similar result was obtained by other workers[78] who subjected specimens of cubic vanadium monoxide VO_x (x = 0.86–1.23) to a pressure of 60 kbar and T = 1300° under static conditions. The results of these experiments[78] are given in Table 8; the lattice period increases considerably, and the degree of defect character of the phase decreases. An interesting feature is that, in spite of the high pressure and temperature of treatment (p = 56.4 kbar, t = 1650°), the lattice period of the monoxide NbO (which can be regarded as crystallising in a NaCl structure with 25% ordered vacancies) remains unchanged[67].

Stable zirconium and tantalum monoxides cannot be synthesised under ordinary conditions (vacuum or inert medium, high temperatures).[79] Zainulin and coworkers[80] attempted to prepare ZrO and TaO. The experiments were carried out at p = 77 kbar and t = 800–1250° for 10 min under static conditions in a standard compartment[81]. Specimens of the corresponding oxides were first heated at a reduced pressure of 1.3×10^{-7} mmHg and t = 1400° for 10 h, after which the resuling powders were placed in cylinders of Ta (for the TaO specimen) or zirconium (for the ZrO specimen). The products of the reaction of the mixture of Ta and Ta_2O_5 contained an unknown phase, which crystallised in the orthorhombic system (a = 11.35 Å, b = 8.199 Å, c = 8.396 Å). The mixture of Zr and ZrO_2 treated at 950° contained small quantities of a cubic phase isostructural with NbO. Comparison of the volumes (V) of the starting materials and final products of the reaction $Zr + ZrO = 2ZrO$ ($-\Delta V/V$ = 4.9%) and $3Ta + Ta_2O_5 = 5TaO$ ($-\Delta V/V$ = 12.2%) showed that these reactions should take place with a decrease in V. It was therefore suggested[80] that it is possible in principle to obtain the monoxides TaO and ZrO at high p and t.

V. OXIDE CARBIDES AND OXIDE NITRIDES

Specimens of the cubic oxide carbide $TiC_{0.44}O_{0.57}$ and oxide nitride $TiN_{0.37}O_{0.51}$ have been subjected to all-round compression under quasi-hydrostatic conditions at p = 90 kbar and t = 620–1400° (Table 9).[82] The lattice periods of the specimens of the oxide carbide and oxide nitride treated at p = 90 kbar and t = 1200–1400° are significantly greater than the original values (Table 9). This result, together with the results of the pyknometric determination of the densities, led to the conclusion[82] that the structural vacancies in the unit cell of these phases are filled. An interesting feature is that in the oxide carbide $TiC_{0.44}O_{0.57}$, both sublattices are complete, whereas in the oxide nitride only the metal sublattice is completely filled. There are no other published data on the influence of high p and t on the characteristics of phases of this kind.

Table 9. Change in the structural characteristics of titanium oxdie carbide and oxide nitride under the influence of pressure p = 90 kbar and different temperatures[82].

Composition and characteristics of original phase	t, °C	Duration of treatment, min	Phase compn. of compressed specimen	Type of lattice	Lattice period, A	No. of formula units (n) in the cell
$TiC_{0.44}O_{0.57}$; a=4.2910 A; n=3.70	620	3	single-phase	FCC*	4.2912	3.70
ditto	1200	1	single-phase	FCC	4.308	3.98
$TiN_{0.37}O_{0.51}$; a=4.2270 A; n=3.82	700	2	two phases of the same type	FCC	4.21 4.23	—
ditto	1200	4			4.239	3.99
»	1400	2	single-phase single-phase	FCC FCC	4.2448	4.00

* Face-centred cubic

VI. SUMMARY

Before discussing the above results, it is appropriate to mention briefly one of the component parts of Kurnakov's theory of daltonides and berthollides—the concept of "imaginary" compounds[83]. Kurnakov, in an examination of the chemical character of berthollides, postulated the following possible treatments:

a) berthollides are definite compounds in a state of dissociation;

b) berthollides are solid solutions of definite compounds, unstable in the free state;

c) berthollides are solutions of polymorphic modifications of the components, unstable in the free state.

The term definite compounds is here understood to mean chemical compounds of constant composition, which obey the law of simple and multiple proportions. In accordance with this, Kurnakov proposed three types of equilibrium diagram (Fig. 1). The compounds AB_n, AB_{n_1}, AB_{n_2} which are unstable in the free state and which obey

the laws of stoichiometry, and the modification of the component B_1, were later, at Ageev's suggestion[83,85], called "imaginary". Kurnakov, referring to the method of finding imaginary compounds and modifications, warned that considerable difficulties are encountered in attempts to distinguish these cases experimentally; this can be done only tentatively, by comparing with analogous systems in which the singular ordinate AB_n (Fig. 1*b*) or the second modification (B_1) of the component B (Fig. 1*c*) can be observed directly. In other words, it is necessary to assume the existence, in a given system A–B, of an imaginary compound AB_n, AB_{n_1}, AN_{n_2} or an imaginary modification B_1 if these phases are present in an analogous system.

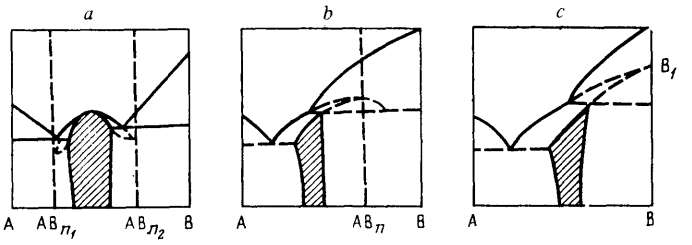


Figure 1. Types of equilibrium diagram with imaginary compounds and an imaginary modification of a component according to Kurnakov, formed: *a*) by isomorphous mixing of non-existent compounds or definite compounds unstable in the free state, AB_{n_1} and AB_{n_2}; b) from a compound AB_n which is unstable or non-existent in pure form; *c*) from a second (B_1) modification of component B, unstable in the free state.

Subsequently, these ideas of Kurnakov were developed in detail by many workers (see for example Refs. 83–97). The nature of imaginary compounds not realised under ordinary conditions was first developed from the structural viewpoint by Bokii[91]. Bokii regarded berthollides as phases of variable composition, in which the limiting degree of filling of the regular system of points (RSP) of the structure is not achieved. In other words, if the processes of substitution, introduction, and removal of atoms under given experimental conditions do not reach the limits characteristic of a given structure, the limiting rational composition is not realised in these phases. In Bokii's opinion, this composition, corresponding to the imaginary compound, can readily be determined by extrapolating the curve characterising the change in the RSP to the composition at which the RSP is completely filled (although this composition will lie beyond the limits of the homogeneity range). It should be noted that in Kurnakov's work[83], for berthollides with and without a maximum on the "composition–property" diagram, two (Fig. 1*a*) and one (Fig. 1*b*) limits respectively were noted, corresponding to the imaginary compound. According to Bokii[91], however, any curve (on the "composition–property" diagram) which does not end at a component or at a compound can be continued in both directions as far as the corresponding compound. In Kurnakov's opinion, the determination of the composition of imaginary compounds on the "composition–property" curve requires the availability of the maximum number of points (in order to carry out the extrapolation over the shortest possible distance), whereas according to Bokii[91], the composition of the imaginary compound can readily be determined from only one point, and the position on the curve, characterising the change in the RSP, at which this extremal point is situated is not important. It is only in the case of a berthollide with a maximum that it is necessary to use two points, since the change takes place in two RSP.

From the foregoing, and with allowance for the ideas put forward by Zainulin and coworkers[82], it is possible to explain various results obtained using high pressures and temperatures, in particular data[49,52,53,65–67,71–73,82] which indicate broadening of the homogeneity range of various phases. Thus stoichiometric cubic (NaCl type) molybdenum carbide, synthesised at high p and t and unstable under ordinary conditions, is the limiting compound at which the RSP is completely filled. In this connection, from data obtained[49] at high p and t, the upper limit of the range of existence of the phase MoC_x must be assigned the composition $MoC_{1.0}$ (under ordinary conditions, the carbide $MoC_{0.76}$ is obtained[50,51]).

A composition close to the limiting composition is observed[98,99] for cubic rhenium carbide ReC (a = 4.005 Å), synthesised at p = 160–180 kbar and t = 1000° (τ = 2–5 min), which cannot be obtained under ordinary conditions. For various monocarbides of metals of sub-groups IVa–VIa, the compositions with the maximum saturation by carbon correspond to the formula $MC_{<1.00}$. The composition $MC_{1.00}$ for these compounds can also be realised at high p and t. It may be noted that the specific values of p and t required to achieve the limiting composition with respect to non-metals cannot always be chosen immediately. Thus in the opinion of Boiko and Popova[61], the composition of cubic tantalum nitride, obtained for the first time, is not stoichiometric; this is also indicated by other data[62].

This in the case of carbides and nitrides with the NaCl structure, the maximum concentration of the non-metal is characteristic of the compositions $MC_{1.0}$ and $MN_{1.0}$ (or, with allowance for complete filling of the RSP, M_4C_4 and M_4N_4). The question of the lower boundary of the homogeneity range of these phases is of interest. From structural considerations[91], for the NaCl structure it should correspond to the compositions $M_2X(M_4X_2)$ or, less probably, M_4X. (The carbide Nb_4C has been obtained[100], but its formation is apparently due to impurities). It should be noted that the carbide $TiC_{0.5}$ [101] and the nitrides $TiN_{0.42}$ [102] and $ZrN_{0.5}$ [103] can be obtained even under ordinary experimental conditions. However, there are as yet no data on carbides and nitrides of analogous composition for other transition metals, synthesised at high p and t. As noted by Bokii[91], the width of the homogeneity range of a phase naturally is not always determined by purely structural factors; it is also influenced by the valency state of the atoms.

Mention must also be made of the oxides of various refractory metals. As already noted, at high temperatures and pressures, increase in these parameters leads to an increase in both the lattice period of the phases TiO_x and VO_x and their densities (for a given composition), due to the filling of the vacancies in the unit cell of the monoxides. Here, however, there is also a change in the charge state of the atoms. In fact for example, the complete monoxide $TiO_{1.00}$, in

contrast to the defect structure apparently contains no M–M bonds, since the M atoms are completely shielded by oxygen atoms[104]. The X-ray emission spectra of compressed specimens of $TiO_{0.88}$ (90 kbar, 1200°, 3 min) and $TiO_{1.27}$ (90 kbar, 1240°, 1 min) also indicate a change in the charges on the atoms[105].

In Batsanov's opinion[54], a change in the charge is also responsible for the increase in the lattice periods of NdF_3 after shock compression (a_{init} = 7.035 Å, c_{init} = 7.211 Å, a_{compr} = 7.066 Å, c_{compr} = 7.230 Å). Batsanov also gave the same explanation for the observed increase[105] in the lattice periods of Co and Ni subjected to dynamic compression.

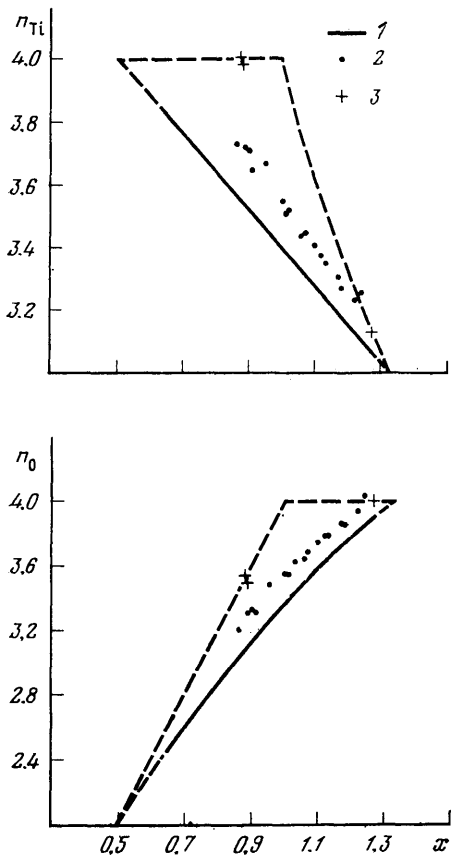


Figure 2. Limits of the change in the degree of filling of the unit cell of the phase TiO_x (range of existence of electronic modifications of titanium monoxide); *1*) data from Ref. 79 for the phase TiO_x synthesised under ordinary conditions; *2*) and *3*) data from Refs. 67 and 72 for the phase TiO_x obtained at high *p* and *t*.

In the homogeneity range of titanium monoxide[82,97], it is possible to distinguish three imaginary compounds: $Ti_2O(Ti_4O_2)$, Ti_3O_4, and $TiO_{1.0}(Ti_4O_4)$ with filled metal, non-metal, and both sublattices respectively. The compounds Ti_3O_4 and Ti_4O_4 can be regarded as already realised[67,71]. As far as the compound $Ti_2O(Ti_4O_2)$ is concerned, it has been noted[82] that it may correspond to the cubic phase detected in the decomposition of $TiO_{1.27}$ (90 kbar, 1300°, 2 min). The same imaginary compounds are revealed in the homogeneity range of VO_x. Up to the present, however, it has been possible to synthesise only the monoxide having an almost completely filled non-metal sublattice, with the composition $VO_{1.23}$ [78] (instead of $VO_{1.33}$).

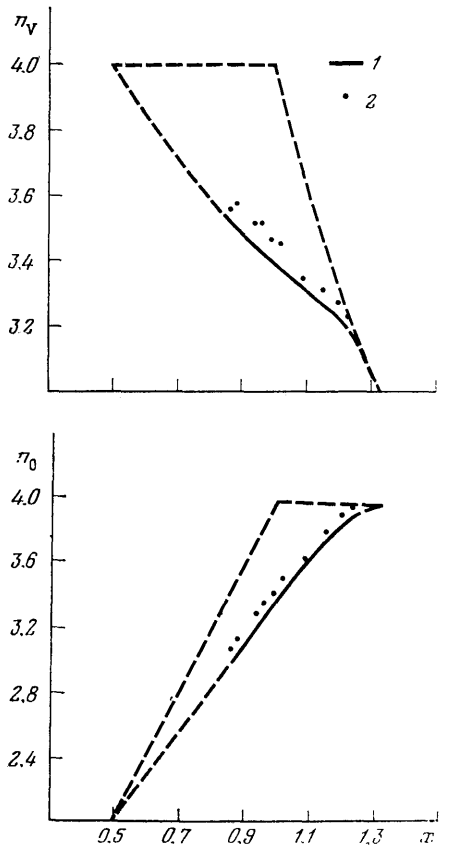


Figure 3. Limits of the change in the degree of filling of the unit cell of the phase VO_x (range of existence of electronic modifications of vanadium monoxide); *1*) data from Ref. 79 for the phase VO_x synthesised under ordinary conditions; *2*) data from Ref. 78 for the phase VO_x obtained at high *p* and *t*.

Thus in the case of phases having dual defect character, it is possible, by filling the structural vacancies in one or both sublattices (by the action of high temperatures and pressures), without changing the composition, to obtain compounds with different concentrations of electrons in the unit cell, that is new electronic modifications.

This feature is illustrated in Figs. 2 and 3. It can be seen that in addition to the imaginary (limiting) compounds (M_4O_2, M_3O_4, M_4O_4), it is possible in the Ti–O and V–O systems to obtain a large number of phases in which the number of particles in the unit cell varies within the ranges indicated in Figs. 2 and 3. If the degree of

completeness changes under the influence of p and t along a straight line parallel to the ordinate (x = const), it follows that in the general case, as far as the limiting degree of filling of one of the sublattices, corresponding electronic modifications of the phase MO_x, which exists under ordinary experimental conditions, are realised successively. This may be followed by decomposition with the liberation of metal (for $x < 1.0$) or oxygen (for $x > 1.0$) or filling by the atoms of the "other" sublattice. In the case of compounds with vacancies in only one of the sublattices, however, filling of the unoccupied positions can take place only with a simultaneous change in composition. In other words, in order to obtain, for example, defect-free FeO it is necessary to introduce a sufficient additional quantity of iron atoms into the lattice of wüstite Fe_xO. This was demonstrated by Katsura and coworkers[65], who synthesised stoichiometric wüstite at p = 36 kbar and t = 770°.

In conclusion, other methods of realising imaginary compounds may be mentioned, for example the use of low temperatures ($t < 0$°C) and high pressures[91] and also the use of super-fast quenching from high temperatures[107]. In addition, cubic tantalum nitride has been obtained[108] by treating the metal in an atmosphere of nitrogen, ionised by a glow discharge, at $t > 1600$°. Finally, Bokii[91], following Kurnakov[83], considers that imaginary compounds can be obtained using chemical additives. This possibly applies to the cubic (NaCl type) carbide Nb_4C, synthesised by Umanskii[100]. Finally, the possibility of obtaining chemical compounds of this type by ion implantation is not excluded (see for example Ref. 109). A large number of imaginary compounds, including those predicted by Ageev[84,85], may also be realised by the methods described above, in addition to the use of high temperatures and pressures.

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